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Ferriferous orthoclase from Madagascar.

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Introduction.

In 1916 Kôzu recorded the fact that a specimen of yellow Madagascar orthoclase, subsequently shown by Seto (1923) to contain 2·93% Fe_2O_3, had an optic axial angle of 20° 17′ (Na_D light) with the optic axial plane parallel to (010). This observation is in apparent conflict with the useful curves relating 2V to composition for alkali-felspars compiled by Dr. O. F. Tuttle (1951, 1952). These curves were designed to show how the felspars fall into several more or less distinct series, rather than as an aid to the precise determination of composition, which in fact must be decided by other means. The possibility of transitional forms between the series was clearly recognized (e.g. 1952, p. 565). Under the stimulus of a visit by Dr. Tuttle to Cambridge in 1951 it was decided to investigate the anomalous properties of the Madagascar felspars in relation to their iron content and further to test the effect of iron on the d ($\bar{2}01$) powder method for the determination of the compositions of alkali-felspars

(Bowen and Tuttle, 1950). At first it seemed likely that there is a direct relationship between optic axial angle (and orientation) and iron content. However, after detailed study of sixteen crystals from the one locality it now appears that specimens with the optic axial plane parallel to (010) are in fact to be regarded as high-temperature modifications approximating to Tuttle's 'high-temperature sanidine' series. These presumably have a largely disordered arrangement of the Si and Al atoms (cf. Barth, 1934; Cole, Sörum, and Kennard, 1949; Laves, 1952). A transition tending towards common orthoclase is recognized on the basis of intermediate optic axial angles and lattice dimensions. The effect of iron seems to be to promote the stability of the sanidine modification. Some remarks are made in an appendix on the excellent d ($\bar{2}01$) method for the determination of the composition of alkali-felspars.

Previous work.

Yellow orthoclase of gem quality from Itrongay, near Fianarantsoa, Madagascar, was first described by Lacroix (1912), who states that the crystals come from a miarolitic pegmatite which also contains quartz, transparent diopside, adularia, apatite, chalcedony, and opal. Outcrops of the pegmatite are small, but its constituents are abundant on the surface as crystals and broken fragments in part enclosed in a calcareous tufa of recent formation. Lacroix observed that the density and other properties were variable, and when in 1913 he published an analysis showing 2·88 % Fe_2O_3, he suggested that ferric iron replaces equivalent amounts of aluminium within the structure. This suggestion has met with general acceptance. In 1922 Lacroix commented on the similarity to sanidine in optic orientation, but he contended that, unlike sanidine, the Madagascar orthoclase is a pegmatite mineral of relatively low-temperature formation.

Owing no doubt to the high quality of the Itrongay crystals, at least nine analyses of them have been published from time to time and specimens have been used by numerous workers in experiments on the properties of felspars. Following the observations of Kôzu (1916), a series of three analyses made by Seto (1923) showed a relation between depth of colour, iron content, and refractive indices. Kôzu and Saiki (1925) investigated the thermal expansion of the mineral, and Kôzu and Suzuki (1925), Barth (1931), and Spencer (1930, 1937) have all used specimens in experiments on the influence of heat on the optic axial angle. Lacroix himself (1912) observed that the yellow colour is unchanged on prolonged

heating at red-heat. Powders have been X-rayed by Ito and Inuzuka (1936), and by Osten (1951), and the approximate cell size of Spencer's specimen 'A' was determined by Chao, Smare, and Taylor (1939). Six existing analyses were brought together by Faust (1936), who carried out a study of the melting relations of pure synthetic iron-orthoclase. Various other writers, such as Alling (1923) and Rosenquist (1951), have commented on the Itrongay felspars in the course of discussions on the entry of iron into the felspar structure.

Material.

The material available for study consisted of six crystals from the museum of the Department of Mineralogy and Petrology, Cambridge; two provided by Mr. B. W. Anderson of the gemmological laboratory of the London Chamber of Commerce; and a fine collection of about a dozen crystals provided by Professor M. Roques of Clermont-Ferrand. In addition, small fragments of Spencer's specimen 'A' were used for X-ray powder photographs. All the crystals studied are broken fragments, but no. 1 shows a combination of the forms {010}, {110}, {130}, and {20$\bar{1}$}. In each case there is a particularly conspicuous basal cleavage, and a less perfect cleavage parallel to (010). The colour varies from very pale yellow to deep amber-yellow and is clearly related to the iron content. With one exception all the crystals studied in detail are perfectly clear and transparent and appear to consist of one phase only. The exception, no. 14, shows a pearly schiller due to cryptoperthitic lamellae sub-parallel to (100) and it is also interesting on account of the presence of fluid-and-bubble inclusions in the form of negative crystals.

Chemical composition.

Three analyses from the literature that are accompanied by optical data are reproduced in table I together with two new analyses by Mr. J. H. Scoon. In each case compositions are recalculated to weight per cent. of the components orthoclase, iron-orthoclase ($KFeSi_3O_8$), albite, and anorthite. Following Faust (1936), small amounts of FeO are treated as Fe_2O_3. Ferric iron can be accounted for in the felspar structure more easily than can ferrous, since in so many minerals Fe^{+3} (ionic radius 0·67 Å.) readily replaces Al^{+3} (0·57 Å.). Some further slight justification for the course here followed comes from the fact that the small amounts of FeO reported in some analyses are at most not much greater than the blank likely to be encountered in a normal FeO

TABLE I. Analyses and optical properties of ferriferous Madagascar alkali-felspars.

	2.	6.	A.	S1.	S2.
SiO_2	64·94	64·76	64·40	64·25	64·21
TiO_2	nil	nil	—	—	—
Al_2O_3	16·74	17·22	18·70	16·06	17·78
Fe_2O_3	2·56	1·50	0·62	2·93	1·15
FeO	nil	nil	0·09	0·25	0·09
MnO	nil	nil	—	—	—
MgO	0·04	0·04	trace	nil	nil
CaO	0·03	0·06	trace	trace	0·07
Na_2O	0·79	0·47	0·46	0·44	0·42
K_2O	15·33	16·00	16·14	16·15	15·21
H_2O-	nil	nil	—	—	—
	100·43	100·05	100·41	100·08	'99·63'
Recalculated composition, weight per cent.					
Or	83·3	89·9	93·3	84·0	90·7
Fe-Or	9·8	5·8	2·8	12·3	5·1
Ab	6·8	4·0	3·9	3·7	3·8
An	0·1	0·3	—	trace	0·4
Optical properties (Na_D light).					
α	1·5265	1·522	1·5194	1·5216	1·5185
β	1·531	1·5265	1·5237	1·5259	1·5225
γ	1·5315	1·5265	1·5241	1·5261	1·5239
$2V_\alpha$ (observed range) ...	32–33½°	11½–17°	—	—	—
$2V_\alpha$ (average)	32½°	13½°	34·8°	20° 17′	—
Optic axial plane ...	∥(010)	⊥(010)	⊥(010)	∥(010)	—
Dispersion	$v > r$	$r > v$	$r > v$	$v > r$	—
α:a in obtuse angle β ...	5°	5½°	5·2°	—	—
After treatment at 1075° C.					
$2V_\alpha$	55°	55–56°	53·8°	—	—
Optic axial plane ...	∥(010)	∥(010)	∥(010)	—	—
Dispersion	$v > r$	$v > r$	$v > r$	—	—

2. Amber-yellow crystal. New analysis by J. H. Scoon.
6. Pale yellow crystal. New analysis by J. H. Scoon.
A. Spencer 'A', 1937. E. Spencer, anal.
S1. Kôzu, 1916; Seto, 1923. K. Seto, anal.
S2. Lighter colour than S1. Seto, 1923. K. Seto, anal.

determination. Mr. Scoon reports that no appreciable amounts of FeO are present in the two specimens analysed by him. The fact that Fe^{+3} does actually replace Al^{+3} in the felspar structure was adequately demonstrated by Faust and is supported by atomic formulae calculated from the new analyses thus:

no. 2, $(K_{0.90}Na_{0.07})(Al_{0.91}Fe_{0.09})Si_{3.01}O_8$,
no. 6, $(K_{0.95}Na_{0.04})(Al_{0.94}Fe_{0.05})Si_{3.01}O_8$.

Partial analyses for iron (table II) have been carried out on thirteen crystals, three of them by Mr. Scoon using the thioglycollic acid colorimetric method, and the remainder by the writer using a method involving reduction and titration, supported in many cases by separate colorimetric estimations. The plagioclase component has been estimated by X-ray methods as described later.

TABLE II. Partial analyses of yellow Madagascar orthoclases and optical properties.

	1.	3.	4.	5.	7.	9.	10.
Fe_2O_3 %	2·0	1·45	0·9	n.d.	1·25	3·25*	2·60*
$KFeSi_3O_8$ weight %	7·7	5·6	3·5	n.d.	4·8	12·5	10·0
(Ab+An) % by $d(\bar{2}01)$	4	6	4	0	2	0	1
Refractive indices α	1·5245	1·523	1·521	1·521	1·522	1·5285	1·526
β	1·529	1·5275	1·5255	1·5255	1·5265	1·532	1·530
γ	1·5295	1·5277	1·526	1·5255	1·5265	1·533	1·531
$2V_\alpha$ observed range	25½–39°	12½–23½°	33–35½°	12½–22°	3–22°	49–51°	44–48°
$2V_\alpha$ average	28°	18°	35°	17°	13°	50°	45½°
Optic axial plane	∥(010)	⊥(010)	⊥(010)	⊥(010)	∥(010)	∥(010)	∥(010)
Dispersion	$v > r$	$r > v$	$r > v$	$r > v$	$v > r$	$v > r$	$v > r$
Properties after heating at 1075° C. for 160 hours.							
$2V_\alpha$	—	—	—	—	—	60½°	—
Optic axial plane	—	—	—	—	—	∥(010)	—
Dispersion	—	—	—	—	—	$v > r$	—

	11.	12.	13.	14.	15.	16.
Fe_2O_3 %	1·52*	1·4	0·5	1·5	1·7	0·5
$KFeSi_3O_8$ weight %	5·9	5·4	1·9	5·8	6·6	1·9
(Ab+An) % by $d(\bar{2}01)$	3	1	3	9†	7	4
Refractive indices α	1·5225	1·5225	1·520	1·5235	1·5235	1·520
β	1·5265	1·5265	1·5235	1·5275	1·5275	1·524
γ	1·527	1·527	1·524	1·528	1·528	1·5245
$2V_\alpha$ observed range	22–31°	22–33°	34–35°	21½–24½°	23½–25½°	34½–36°
$2V_\alpha$ average	26°	25°	34½°	23°	24½°	35½°
Optic axial plane	∥(010)	∥(010)	⊥(010)	⊥(010)	⊥(010)	⊥(010)
Dispersion	$v > r$	$v > r$	$r > v$	$r > v$	$r > v$	$r > v$
Properties after heating at 1075° C. for 160 hours.						
$2V_\alpha$	50½–54½°	—	—	51°	51°	—
Optic axial plane	∥(010)	—	—	∥(010)	∥(010)	—
Dispersion	$v > r$	—	—	$v > r$	$v > r$	—

Extinction angle $\alpha:a$ in obtuse angle $\beta = 5\frac{1}{2}° \pm \frac{1}{2}°$ in each case.

* J. H. Scoon, analyst.

† Cryptoperthitic $(Ab+An)_5$ for orthoclase component before homogenization.

REFRACTIVE INDICES.

Refractive indices for the newly analysed crystals and for Spencer 'A' are plotted in fig. 1 and the dependence of the indices on the iron content is immediately apparent. In a few cases the indices in different parts of the one crystal were found to vary by amounts up to 0·003 and in such cases mean figures are quoted. As the combined content of albite and anorthite is shown by chemical analysis and by powder photographs to be rather uniformly low, variations in indices from this factor should be correspondingly slight. From the refractive index graphs of Tuttle

(1952, fig. 2) it can be seen that an albite content of 9 %, the highest observed in the Madagascar collection, would raise the indices by about 0·001 relative to albite-free members. An increase of refractive index

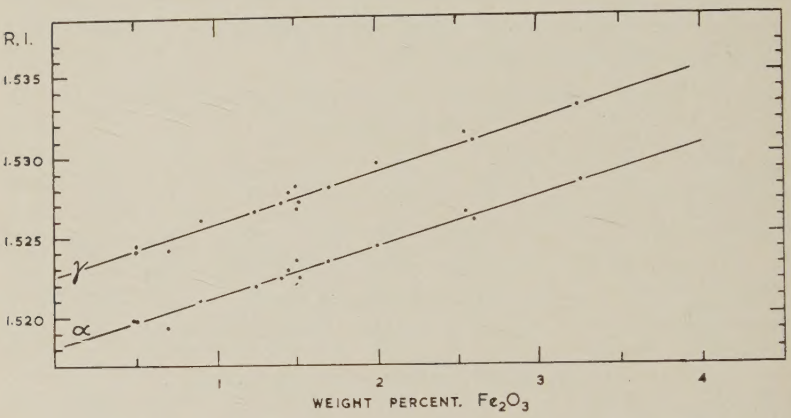

Fig. 1. Refractive indices of ferriferous orthoclase.

with iron content is of course to be expected, and Gaubert (1926) has given the figures α 1·601, γ 1·609 for the synthetic iron-orthoclase prepared by Hautefeuille and Perrey (1888).

Heat-treatment.

Spencer (1937) found that on prolonged heating at 1075° C., the optic axial plane of his specimen 'A' was brought into (010) with 2V 53·8°. Constancy was reached in a little over one hundred hours. At 1120° C. the angle attained was found to be 58°. These properties for the heated natural felspar are those of 'high-temperature sanidine' (Tuttle, 1952). By heating specimens for shorter periods at lower temperatures, Kôzu and Suzuki (1925) and Barth (1931) were able to produce rather smaller changes.

After 2V had been determined on oriented plates of six of the crystals used in the present study, parts were detached and were heated for 160 hours at 1075°±10° C. In each case the optic axial plane after treatment was found to be parallel to (010) with 2V 50–60° (tables I and II). Two specimens, nos. 2 and 6, were given a preliminary heating for 110 hours at 1050–1060°. No. 2 had already reached a value of 55°, but no. 6 had an optic angle of only 45–48°, which increased during subsequent heating to 55–56°.

Optic axial angle.

Plates $\frac{1}{2}$–1 mm. thick were cut through each crystal in a direction approximately at right angles to the acute bisectrix. The optic axial angle was measured over this surface on the universal stage, using interference figures to locate the optic axial points with a precision of $\pm\frac{1}{4}$–$\frac{1}{2}°$ (tables I, II, fig. 2). The measured angles were found to be variable, in one case over as much as 19°. In some cases the variation

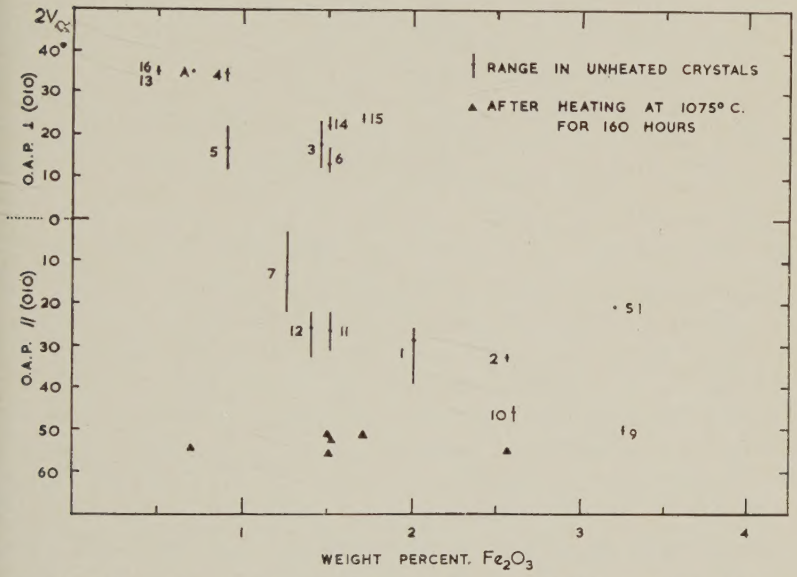

Fig. 2. Optic axial angle plotted against iron content for ferriferous orthoclase from Madagascar.

could conceivably be due to zoning, but in nos. 5 and 7 especially, 2V varies across the section in a curious blotchy manner quite incompatible with compositional zoning. In order to minimize the effects of any variation in composition that might occur, the analysed samples were taken from material adjacent to that studied optically.

Strong dispersion of the optic axes is evident in the interference figures of the iron-rich members (cf. Kôzu, 1916) and the dispersion scheme $v > r$ when the optic axial plane is parallel to (010) and $r > v$ when it is perpendicular to (010), provides a check on the optic orientation as determined by other means.

A glance at fig. 2 shows that there is a tendency for the crystals with

highest iron content to have their optic axial plane parallel to (010), and in fact this is the case for all five crystals with not less than 2 % Fe_2O_3 (7·7 % $KFeSi_3O_8$). At first it appeared that the iron content directly controls 2V and the optic orientation, but when more crystals became

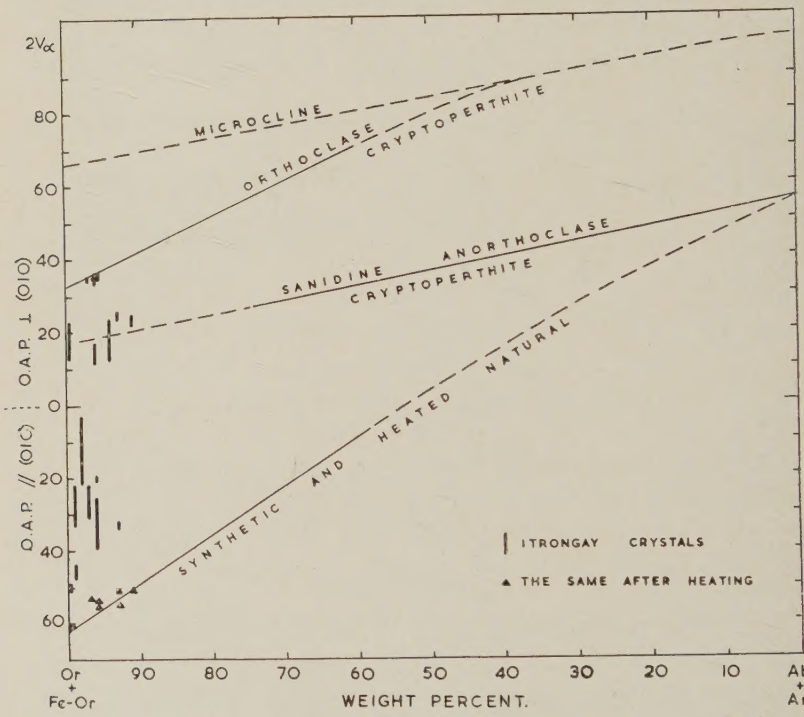

FIG. 3. Graph showing relation between 2V and composition of several series of alkali-felspars (after Tuttle, 1952, fig. 1). Tuttle stresses that the range of values for 2V for natural felspars, as shown in his original diagram, precludes the use of the graph for determination of composition. Data are added for the ferriferous felspars of Itrongay to show the range of intermediate values observed.

available for study, this simple hypothesis became untenable for the following reasons:

(i) Irregular variation in 2V occurs in single crystals, through as much as 19° as already noted.

(ii) Separate crystals with essentially the same chemical composition sometimes vary between themselves in even greater amount. Thus the group 3, 6, 11, and 12, all with approximately 1·5 % Fe_2O_3 and closely

comparable refractive indices and albite contents, have optic axial angles reaching $23\frac{1}{2}°$ perpendicular to (010) and 33° parallel to (010). There is in effect a difference here of $56\frac{1}{2}°$ in the optic axial angle of material of similar composition.

For these reasons it appears that any control that iron content exerts on 2V is imperfect and probably indirect. Furthermore, in the case of the heat-treated material the effect of iron is clearly shown to be small and when the small albite contents are considered the determinations of 2V are found to fall very close to the curves for sanidinized alkali-felspars given by Spencer (1937, fig. 2) and Tuttle (1952, fig. 1), as shown in fig. 3.

Irrespective of iron content, an almost continuous series of values has been observed for the unheated crystals, the actual range noted being 2V 3–51° with the optic axial plane parallel to (010), and 2V $11\frac{1}{2}$–$25\frac{1}{2}°$, 33–36° when it is perpendicular to (010).

Correlation between lattice spacings and optic axial angle.

During the inspection of powder photographs of Itrongay felspars it became evident that heat-treatment produces conspicuous changes in the region of the two strong lines that occur close together in the region of 3·2 to 3·3 Å. In unheated material such as Spencer 'A' they consist of an unresolved doublet 002, 040 and another doublet $\bar{2}02$, 220 which is usually resolved in good quality photographs taken on a 19-cm. camera with copper radiation, and which is very clearly resolved on an X-ray spectrometer chart demonstrated to the writer by Dr. W. S. MacKenzie. Upon heat-treatment, the strongest components 002, 220 move farther apart, $\bar{2}02$ is clearly visible between them, and 040 less readily so. Systematic changes in positions of certain other reflections can also be traced. Cole, Sörum, and Kennard (1949, p. 282) showed that on sanidinization of the orthoclase Spencer 'C', the *c*-axis was reduced in length, whereas *b* increased and *a* underwent little change. Furthermore, they pointed out (p. 287) that the changes are in the direction to be expected if sanidinization is due to a disordering process of Al atoms from Si_1 to Si_1 and Si_2 positions. It follows from the cell dimensions given that sanidinization must result in an increase in the angular separation of the 002 and 220 reflections in powder diagrams. Thus for Cu-$K\alpha$ radiation, $2\theta_{(002)}-2\theta_{(220)}$ (calculated) = 0·66° for unheated Spencer 'C', increasing to 0·76° for the heated material. This corresponds to the observed behaviour of the Itrongay felspars.

Now if the ferriferous felspars with small optic axial angles represent

intermediate stages in a transition from 'high-temperature sanidine' with 2V 50–60° parallel to (010), to common orthoclase which for the moment we can consider as having 2V 35° perpendicular to (010), then one might expect that their lattice dimensions would also have intermediate values. With an ordinary powder camera the angular separation of adjacent lines can often be measured with greater accuracy than can the absolute value of 2θ. As the differences in lattice dimensions involved in the present problem are small, it is convenient to study them by means of such angular separations of adjacent lines, and since c decreases on sanidinization whereas b increases, the differential movement of pairs such as 002, 040 should be specially suitable for investigation. These particular reflections are not sufficiently well resolved, however, to allow their study, so data are presented in table III and fig. 4*a*, *c* for

TABLE III. $\Delta 2\theta$ values for ferriferous orthoclase from Itrongay, Madagascar, and for synthetic $KAlSi_3O_8$. (Cu-$K\alpha$ radiation, 19-cm.-diameter powder camera.)
$\Delta 2\theta_1$: $2\theta_{(040,002)} - 2\theta_{(220)}$ or $2\theta_{(002)} - 2\theta_{(220)}$.
$\Delta 2\theta_{1a}$: The same adjusted towards zero plagioclase content.
$\Delta 2\theta_2$: $2\theta_{(11\bar{2})} - 2\theta_{(130)}$.

A. *Unheated:*

Specimen	(Ab+An).*	Op. ax. pl.	$2V_\alpha$ (av.)	$\Delta 2\theta_1$.	$\Delta 2\theta_{1a}$.	$\Delta 2\theta_2$.
1	4	∥(010)	28°	0·71°	0·75°	2·175°
2	5	∥(010)	32½	0·68	0·73	2·14
3	6	⊥(010)	18	0·65	0·71	2·12
4	4	⊥(010)	35	0·65	0·69	2·12
5	0	⊥(010)	17	0·68	0·68	2·15
6	1	⊥(010)	13½	0·71	0·72	2·155
7	2	∥(010)	13	0·73	0·75	2·18
9	0	∥(010)	50	0·77	0·77	2·17
10	1	∥(010)	45½	0·745	0·755	2·16
11	3	∥(010)	26	0·72	0·75	2·185
12	1	∥(010)	25	0·73	0·74	2·17
13	3	⊥(010)	34½	0·675	0·705	2·14
14	5	⊥(010)	23	0·645	0·695	2·115
15	7	⊥(010)	24½	0·62	0·69	2·115
16	4	⊥(010)	35½	0·67	0·71	2·125
Spencer 'A' ...	4	⊥(010)	34·8	0·635	0·675	2·115

B. *Heated 160 hours at 1075° C., and synthetic:*

9	0	∥(010)	60½°	0·85°	0·85°	2·295°
11	3	∥(010)	52½	0·83	0·86	2·26
14	9	∥(010)	51	0·80	0·89	2·24
15	7	∥(010)	51	0·77	0·84	2·245
Spencer 'A' ...	4	∥(010)	53·8	0·82	0·86	2·29
$KAlSi_3O_8$† ...	0	∥(010)	60	0·87	0·87	2·28

* (Ab+An) estimated by d ($\bar{2}01$) method.
† X-ray data from Donnay and Donnay (1952, p. 124).

$2\theta_{(11\bar{2})} - 2\theta_{(130)}$ and for the separation of the two conspicuous strong lines referred to above. In the latter case, interpretation is complicated by the imperfect resolution of the constituent doublets, but in general the angles refer to $2\theta_{(002,040)} - 2\theta_{(220)}$ in the case of unheated specimens and to $2\theta_{(002)} - 2\theta_{(220)}$ for heat-treated and synthetic material. The angular

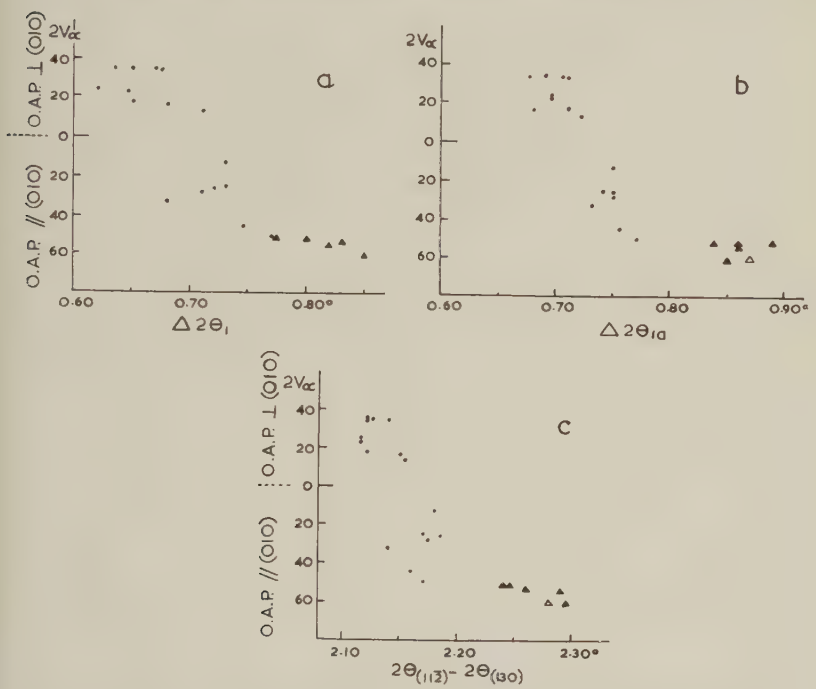

FIG. 4. $\Delta 2\theta$ for pairs of powder lines of alkali-felspars as a function of 2V (see table III). *Points*: Ferriferous orthoclase, Itrongay, Madagascar. *Solid triangles*: The same after heating to 1075° C. for 160 hours. *Open triangles*: Synthetic $KAlSi_3O_8$. Cu-$K\alpha$ radiation.

separation of these strong lines has been shown by Osten (1951) to vary with albite content. The data of Donnay and Donnay (1952, pp. 124, 125) indicate that $2\theta_{(002)} - 2\theta_{(220)}$ for synthetic monoclinic alkali-felspars decreases at the rate of approximately 0·01° for every 1 % albite. In an attempt to adjust the present measurements towards a constant, albite-free basis (fig. 4*b*), $2\theta_{(002)} - 2\theta_{(220)}$ (or $2\theta_{(002,040)} - 2\theta_{(220)}$) has therefore been reduced by 0·01° for every 1 % (Ab + An) as estimated by the powder method. Data for synthetic $KAlSi_3O_8$ are added for comparison.

By averaging repeated measurements of peak positions made with a travelling microscope and vernier, reproducibility of about 0·01° in $\Delta 2\theta$ has been attained. In spite of a scatter of points that is rather too great to be ascribed to simple errors of measurement alone, fig. 4 shows that there is a strong correlation between optic axial angle and lattice spacings. As a group, the Itrongay crystals with high-temperature sanidine orientation are seen to be intermediate between those with orthoclase orientation and the heat-treated or synthetic specimens. This is taken as evidence that the anomalous optical properties, such as those recorded by Kôzu (1916), are due to the occurrence of forms transitional between high-temperature sanidine (disordered) and common orthoclase (presumed to be partially ordered). In detail it is seen that the lattice spacings of the transitional specimens tend to be nearer to those corresponding to common orthoclase than to those of the heat-treated or synthetic crystals even where 2V most closely approaches the condition of the latter.

The general conclusions of this section are supported by the consideration of cell dimensions (table IV) calculated from the powder patterns

Table IV. Cell dimensions and 2V of ferriferous felspars and of Spencer 'C'.

	4.	11.	11 (heat-treated).	C.*	C* (heat-treated).
a (Å.) ...	$8{\cdot}58_1$	$8{\cdot}58_6$	$8{\cdot}59_6$	$8{\cdot}561_6$	$8{\cdot}564_2$
b	$12{\cdot}99_0$	$13{\cdot}02_0$	$13{\cdot}03_3$	$12{\cdot}996_2$	$13{\cdot}030_0$
c	$7{\cdot}20_0$	$7{\cdot}18_9$	$7{\cdot}17_9$	$7{\cdot}193_4$	$7{\cdot}174_9$
β	$116{\cdot}0_6°$	$115{\cdot}9_8°$	$116{\cdot}0_3°$	$116{\cdot}01_5°$	$115{\cdot}99_4°$
Op. ax. pl. ...	$\perp(010)$	$\|(010)$	$\|\|(010)$	$\perp(010)$	$\|\|(010)$
$2V_\alpha$	35°	26°	$52\frac{1}{2}°$	43·6°	44·8°

* X-ray data from Cole, Sörum, and Kennard, 1949, p. 282; optical data from Spencer, 1937, plate XVIII.

of three typical Itrongay specimens, chosen for their wide range of 2V yet closely comparable chemical compositions. In the critical b and c dimensions no. 11 (unheated) is seen to be intermediate between no. 4 and no. 11 (heat-treated), as it is also in 2V. Data for Spencer 'C' are added for comparison. A close similarity in behaviour is evident, the only significant difference being that the higher albite content of 'C', 9 % as against an estimated 3 to 4 % in nos. 4 and 11, is reflected in a smaller a-axis. The powder data used for the computation of these cell dimensions are given in table V.

TABLE V. Powder data used in the calculation of cell dimensions (see table IV). Cu-$K\alpha$ radiation, Ni filter.

hkl.	Int.	4.	11.	11 heat-treated.
$\bar{2}01$	4	$\theta = 10{\cdot}513°$	$\theta = 10{\cdot}504°$	$\theta = 10{\cdot}503°$
111	$2\frac{1}{2}$	11·275	11·265	11·277
130	7	11·781	11·760	11·746
$13\bar{1}$	2	12·307	12·303	12·283
$11\bar{2}$	3	12·840	12·852	12·876
220	7	13·444	13·421	13·413
$20\bar{2}$	4	—	(13·56)	(13·57)
040	3	13·769	13·781	(13·70)
002	10			13·828
131	5	14·928	14·904	14·907
$13\bar{2}$	1	(16·17)	(16·165)	(16·18)
$31\bar{2}$	< 1	—	(17·205)	—
$24\bar{1}$	2	17·421	17·394	17·375
112	< 1	—	(17·60)	—
060	3	(20·87)	(20·83)	(20·785)

Angles for inferior reflections in brackets.
The unresolved doublet 041, 022 ($\sim$ 15·4°) and several weaker lines are omitted.
Limits of error approximately 0·01° in θ.

CONCLUDING DISCUSSION.

It has been shown that the variations in 2V and optical orientation of the ferriferous felspars cannot be related directly to the chemical composition, but that both the observed optical data and lattice spacings are compatible with the existence of high-temperature sanidine modifications and transitional forms tending towards common orthoclase. The occurrence of these felspars in a pegmatite is significant in view of the belief sometimes expressed that high-temperature felspars are absent among plutonic associations. A sanidine-bearing pegmatite emplaced in rhyolite-porphyry at shallow depth has also been reported recently (Kelley and Branson, 1947).

A tendency for the most ferriferous felspars (e.g. 1, 2, 9, 10, S1) to have their optic axial planes parallel to (010) has already been noted. Two main hypotheses could be proposed to explain this.

(i) The most iron-rich crystals crystallized as a high-temperature modification, whereas the others crystallized as a low-temperature modification, perhaps, but not necessarily, at a lower temperature. This view makes no allowance for transitional forms and is inadequate.

(ii) All the crystals formed in the high-temperature sanidine condition or in a form approximating to this, and they tended to change over towards common orthoclase. The existence of highly irregular variations in 2V within the one crystal supports the reality of some uncompleted

process of this type. Such a mechanism would be consistent with the view expressed by Laves (1952) that there are two stable modifications of potash-felspar, sanidine stable at high temperatures and microcline stable at low temperatures, and that the former tends to pass towards the latter by an ordering process, with common orthoclase as an unstable intermediate stage.

If the second hypothesis is accepted it follows that a high iron content has tended to inhibit the ordering process. This appears to be a reasonable assumption when it is remembered that the Fe^{+3} ion is larger than Al^{+3}, which it replaces. When the larger Fe^{+3} ions are distributed at random through disordered $AlSi_3$ positions, they might be expected to exert less of a disturbing influence on the felspar structure than if they were concentrated into a restricted number of Al positions as in a fully ordered arrangement. In some interesting experiments using radioactive tracers, Rosenquist (1951) found that up to 0·21 % Fe_2O_3 could enter powdered microcline at 980° C. and much smaller quantities were taken up at lower temperatures. The fact that microcline normally does not carry large amounts of iron in solid solution, although microcline-perthites frequently contain oriented and presumably exsolved lamellae of haematite (Andersen, 1915), indicates the possibility that the ordered structure may be incapable of holding much iron. If so, the presence of iron in a sanidine should have the effect of retarding the ordering process. If ordering is to proceed to the microcline stage (not seen in the Itrongay series) it may be that most of the iron must first be expelled from the lattice. The precise mechanism by which haematite can separate from $KFeSi_3O_8$-bearing felspar remains obscure, and the suggestion by Rosenquist (1951) of complementary introduction of Al_2O_3 poses its own problems. An apparent exception to the above generalization must be recorded. The Palabora microcline, described by Shand (1931, p. 92), contains the relatively large amount of 1·02 % Fe_2O_3.

It remains to consider the question of terminology. Those members with the optic axial plane parallel to (010) are adequately described as sanidine (or high-temperature sanidine). Several crystals have $2V \sim 35°$ and fall near the soda-poor end of the orthoclase curve (fig. 3). However, the only 'orthoclase' with 2V less than 40° available to Spencer (1937) and Tuttle (1952) when they drew up this curve was the ferriferous Spencer 'A' from Madagascar. It is now shown to be associated in its occurrence with sanidines that show more or less continuously variable properties. Hence whether or not Spencer 'A' can be considered as specifically representative of 'orthoclase' is largely a matter of arbitrary

definition, unless it can be shown that the two small gaps in observed 2V are due to causes other than incomplete sampling.

Appendix: Notes on the X-ray-powder method for the determination of alkali-felspars.

Bowen and Tuttle (1950, p. 491) have shown that the measurement of lattice spacings by X-rays, in particular the measurement of d ($\bar{2}01$), affords a very accurate and convenient method for the determination of the composition of synthetic soda-potash-felspars. For the present work the procedure used in the Department of Mineralogy and Petrology, Cambridge, was followed, and synthetic spinel, $MgO.Al_2O_3$ (a = 8·081 A., d (111) = 4·665 A.) was mixed with each felspar to be determined by the powder method in the proportions of 1 part powdered spinel to about 4 or 5 parts felspar. The 111 (spinel) reflection then provides a conveniently placed internal standard line. To avoid the necessity of calculating d ($\bar{2}01$) for each felspar, it is easy to construct for any camera and wave-length a graph from which the composition Or/(Ab+An) can be read off directly from the linear distance on the film between the 111 (spinel) and $\bar{2}01$ (felspar) reflections. Using a 19-cm.-diameter powder camera, filtered Cu-$K\alpha$ radiation, and a low-power travelling microscope, it is possible to measure this distance on good-quality photographs with a precision corresponding to an error of ± 2 % (Ab+An) in the composition. Occasionally it may be necessary to correct for film shrinkage, but errors due to this are usually negligible in the small distance to be measured.

The theoretical basis for the d ($\bar{2}01$) method lies in the fact that the lengths of the a- and c-axes and the angle β all vary in continuous fashion through the series $KAlSi_3O_8$ $NaAlSi_3O_8$ (Donnay and Donnay, 1952, fig. 6; Laves, 1952, fig. 4). The most marked change is a reduction in the length of a. Laves points out that d ($\bar{2}01$) does not depend on the interaxial angles α and γ, and largely for this reason the method is applicable not only to monoclinic felspars but also to triclinic felspars such as anorthoclase. Analysed microclines from Michigan (Klein, 1939) and, after homogenization, Coul More, Loch Assynt (Peach et al., 1907, p. 448) have also been observed by the writer to have $\bar{2}01$ spacings compatible with Bowen and Tuttle's graph (1950, fig. 2).

This determinative graph was constructed for synthetic felspars, in effect 'high-temperature sanidines'. Cole, Sörum, and Kennard (1949) have determined the cell constants for the orthoclase Spencer 'C' and

its sanidinized modification with great precision. Although sanidinization produces significant changes in cell dimensions, the net effect on d ($\bar{2}01$) is slight compared with those changes that accompany varying albite content. Thus it can be calculated that d ($\bar{2}01$) for Spencer 'C' is $4{\cdot}217_3$ and for its sanidinized modification $4{\cdot}217_0$, the difference being negligible and the spacing appropriate for such a felspar containing 9 % (Ab+An). Further confirmation that the Bowen–Tuttle graph may be used to determine the composition of potash-rich low-temperature orthoclase phases in addition to high-temperature synthetic alkali-felspars comes from appropriate and virtually identical direct measurements, before and after heat-treatment, of d ($\bar{2}01$), for Spencer 'C', for the ferriferous Madagascar orthoclases, and for the St. Gotthard adularia Spencer 'B' $(Ab+An)_9$. It may be noted, however, that the d ($\bar{2}01$) curves for high- and low-temperature felspars diverge slightly at the soda-rich end. Thus albite from Amelia, Virginia, with 2·6 % Or, gave the result 4·030 Å., and after inversion to high-temperature albite a distinctly greater spacing, 4·037 Å. Two potash-free authigenic albites from Bellefonte, Pennsylvania (Honess and Jeffries, 1940), and albite from Alp Rischuna, Switzerland (Lewis, 1915), have spacings 4·027 4·029 Å., whereas synthetic high-temperature albite gave 4·034 Å. These variations are near the limit of sensitivity of the methods employed but appear to be significant, high-temperature albite having the greater spacing.

This valuable technique must not be applied without due care. Laves (1952, p. 562) found by single-crystal photographs of certain cryptoperthites that the cell dimensions of the components did not accord with the values found for homogeneous felspars; thus the length of the a-axis of the sodic component of one example indicated the impossible composition of Ab_{110}. Similarly, d ($\bar{2}01$) values determined by the present writer from the powder patterns of the cryptoperthitic moonstones I, J, K, and M described by Spencer (1937) give impossible values of up to 110 % Ab and Or for the sodic and potassic phases respectively. Thus in the case of the homogeneous low-temperature potash-rich felspars examined by the writer, including orthoclase, adularia, and microclines, the Bowen–Tuttle curve gives reliable estimates of composition. The results for the finer orthoclase cryptoperthites, however, do not always conform, as discussed by Laves.

It is important to consider the effect on d ($\bar{2}01$) of components other than orthoclase and albite. It can readily be verified that soda-rich plagioclases have essentially the same $\bar{2}01$ spacings as pure albite and it follows that moderate amounts of the anorthite component have the

same effect on d ($\bar{2}01$) as albite. The total albite plus anorthite is determined. It may be recalled that Tuttle and Bowen (1950, p. 578) and Claisse (1950) have both described powder methods for the determination of certain plagioclases. To test the effect of iron, d ($\bar{2}01$) has been measured for the fully analysed ferriferous orthoclases 2, 6, and Spencer 'A', with 2·56 %, 1·50 %, and 0·62 % Fe_2O_3, respectively. The results for the first two, 4·224 A. and 4·231 A., are 0·004 0·006 A. greater than would be expected for iron-free felspars of corresponding soda content. This would correspond to a possible error by underestimation of about 2–3 % (Ab + An) if the effect of iron-orthoclase was ignored. This effect has not been allowed for in the X-ray determinations of (Ab + An) for the Madagascar felspars given in table II. In the case of Spencer 'A' no significant departure from Bowen and Tuttle's graph was observed. As is to be expected from a consideration of ionic radii, the small amounts of iron encountered in normal felspars, generally less than 0·5 % Fe_2O_3, can have only an insignificant effect on determinations by this method.

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The structures of the plagioclase felspars.

V. The heat-treatment of lime-rich plagioclases.

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Introduction.

THIS work has been primarily concerned with plagioclase felspars within the composition range $Ab_{30}An_{70}$ to Ab_0An_{100}, i.e. felspars with the anorthite-type structure. Some results for less basic specimens will be quoted where appropriate: a fuller description of the effects of heat-treatments on intermediate plagioclase felspars will be published later.

It is convenient in describing the changes which occur in the diffraction patterns to classify the reflections in the following way:

Type (a) $(h+k)$ even, l even	(principal reflections)
„ (b) $(h+k)$ odd, l odd	(subsidiary reflections)
„ (c) $(h+k)$ even, l odd	(subsidiary reflections)
„ (d) $(h+k)$ odd, l even	(subsidiary reflections)

For all specimens, the principal reflections are sharp and are not appreciably changed by heat-treatment: the subsidiary reflections, however, do undergo substantial alterations. In the low-temperature series (Gay, 1953), for pure anorthite, which has a primitive unit cell with c-axis twice the length of that of albite, reflections of all these types are present and sharp. As the percentage of albite is increased, the (c) and (d) type reflections become diffuse and gradually disappear: the specimens examined of composition $Ab_{15\ 20}An_{85-80}$ show only types (a) and (b) reflections, i.e. they still possess the doubled c-axis of the anorthite-type structure but the unit cell, chosen as before, is now body-centred. This structure is observed until a composition of about $Ab_{30}An_{70}$ is reached.

At about this composition the regular periodicity of the structure giving rise to the 14 Å. *c*-axis is destroyed; reflections of type (b), which indicate the doubling of the *c*-axis, are replaced by pairs of reflections symmetrically disposed about the position of the odd layer-lines on *c*-axis photographs from bytownites and anorthites. Recent work by Cole, Sörum, and Taylor (1951) on these intermediate plagioclases suggested that the separation of these subsidiary reflections is a function of composition; they also correlated the separation of these subsidiary reflections on photographs taken about other principal axes with composition.

A number of specimens, some of which occur naturally, do not fit in with this sequence; it is thought that this is due to some special feature of their previous geological history. The difference between the high- and low-temperature forms of albite has been shown quite clearly (Tuttle and Bowen, 1950) and more recently (Laves and Goldsmith, 1951; Gay, 1953) it has become apparent that the structure of pure anorthite is temperature dependent. Very little has been published about the structural changes observed in plagioclases on heat-treatment. This seems surprising in view of the importance of the optical data of Köhler and his co-workers. In the present research, a number of lime-rich plagioclases have been subjected to various heat-treatments and examined by X-ray methods. No detailed optical measurements have been made, since at this end of the series it is known that the optical changes are small and their detection is difficult and uncertain; later, it is hoped to correlate the structural and optical changes. Similar investigations of other composition regions of the plagioclase series are also being undertaken. When these studies are complete, it is hoped that a 'structural phase diagram' can be built up, which will be explicable in terms of changes in the atomic structure of the felspars.

Experimental methods.

(*a*) *Selection and heat-treatment of specimens.*—So far as has been possible, single crystals have been isolated and used in this work. Some of the felspars from which the specimens were taken have been analysed; unzoned grains with extinction angles corresponding to the chemical composition of the bulk material were selected for use. For materials for which no analysis has yet been obtained, the composition was determined optically (no large errors in estimating composition by optical methods will arise at the lime-rich end of the series).

For temperatures up to 900° C. the specimens were heated in a nichrome-wound muffle furnace; a platinum-wound furnace was used for higher temperatures. There is some uncertainty about the exact temperature of heating owing to power input fluctuations.

The duration of heat-treatment was three days. In the present experiments no study of the rates of transformation has been made; it was desired only to find what structural modifications can exist. In transformations of the type found a particular structural state can be attained either by a relatively long treatment at a low temperature or by a relatively short treatment at a higher temperature. However, at the higher temperature, the structural state reached after the short treatment may not be the equilibrium state. In these experiments it was thought best to keep the time of heating constant and use different temperatures.

(*b*) *X-ray methods.*—As far as possible, each series of heat-treatment experiments was carried out on the same single crystal; i.e. each individual specimen was examined in the natural state and after each successive heat-treatment. At each stage oscillation and Weissenberg patterns about the principal axes were obtained; oscillation about other axes has been used sometimes for confirmatory purposes.

Experimental results.

Table I contains a description of the specimens used and their mode of occurrence, together with a brief account of their diffraction patterns after each successive heat-treatment.

In the composition range of the anorthite-type structure, all four classes of reflections can occur. Type (a) reflections are apparently unchanged after any heat-treatment; however, it is probable that there are small changes in their relative intensities which would have become apparent in any detailed structural work. The other three reflection types can be appreciably changed by heat-treatment. Estimates of changes in the diffuseness and intensity of relatively weak spots are difficult to make. The photographs have been taken with identical exposure times, though this does not, unfortunately, ensure strictly comparable photographs. Nevertheless, in some cases it is quite clear that changes have taken place; in other cases it is possible that minor changes in the pattern have occurred but that they remain undetected.

The general trends of the changes are as expected from the earlier work. In the low-temperature series there exists the continuous change

(as the percentage of albite increases) from the primitive pattern to the body-centred pattern, i.e. S → D → A patterns. For pure or almost pure anorthites, although heating at 1100° C. does not apparently lead to any change, heating at temperatures near 1300° C. produces a pattern approaching that from the synthetic material (S → D): this has previously been noted by Laves and Goldsmith (1951). The heating of the least basic specimen showing a well-defined primitive pattern (anorthite, specimen G.C.) shows that the smearing out of the (c) (and (d)) type reflections can occur at a lower temperature (~ 1100° C.); at this temperature with the same period of heating pure anorthite is unchanged. This is to be expected if elevated temperatures and increased soda content act in the same way, as was suggested previously (Gay, 1953). Anorthite M.E. in the untreated state must be regarded as a partially inverted material: no change is observed when this specimen is heated at 1100° C. This may be due to the fact that any increase in diffuseness is relatively small and cannot be detected, or alternatively it is possible that 1100° C. is very close to the temperature from which this specimen was quenched under the conditions of natural occurrence. (This temperature is likely to be too high to sharpen the (c) reflections.)

The transitional material (which shows a D pattern in the low-temperature state) which has been most extensively examined is that from Rum. Here again heating at 1100° C. seems to have no appreciable effect on the pattern, but after treatment at a high temperature (~ 1350° C.) many of the original type (c) reflections have disappeared, leaving only the strongest barely visible and much more elongated (D–A pattern) than those from the pure synthetic anorthite which had effectively been quenched from 1500° C. At still higher temperatures (~ 1400° C.), type (c) reflections have finally disappeared, and type (b) reflections are very much reduced in intensity, although they do not become diffuse (A–bA pattern). It may be possible, with this material, to remove these reflections completely by more prolonged heating or by heating at a higher temperature; so far it has not been possible to carry out experiments of this kind. Bytownite S.2 in the natural condition shows a pattern very similar to that from the Rum specimen; on heating to 1300° C. no detectable change is observed. This seems surprising in view of the marked change in the pattern from the Rum material at a slightly higher temperature; it may be that at this composition the rate of change accelerates rapidly as the temperature is increased.

The Rum material was also heated at temperatures below 1100° C. to see whether the transition from D → S pattern which was found for the

TABLE I. List of specimens and origins with heat-treatments and types of diffraction patterns observed.

Specimen no.	Locality.	Origin.	Anorthite content (mol. %).	Method of determination.	Heat-treatments			Diffraction pattern type			
					1.	2.	3.	Untreated.	Heat-treatment 1.	Heat-treatment 2.	Heat-treatment 3.
Anorthite (S. 20)	—	Synthetic	100	—	3 days at 1100° C.	3 days at 1300° C.	—	D	S	D	—
Anorthite (F. 5)	Pasmeda Alp, Fassa Valley	Veins in limestone block	~100	Optically	3 days at 1100° C.	3 days at 1300° C.	3 days at 1100° C.	S	S	D	S
Anorthite (M.E.)	Miyake, Japan	Volcanic lava	~94	Optically	3 days at 1100° C.	—	—	D Type (c) reflections not so elongated and diffuse as S. 20 untreated.	D Same as untreated.	—	—
Anorthite (G.C.)	Grass Valley, California	Hornblende-norite	92·8	Chemical analysis	3 days at 1100° C.			S This pattern shows type (c) reflections which are effectively sharp though not so well defined as those from specimen F. 5.	D Type (c) reflections showing only slight diffuseness and elongation.		—
Bytownite-anorthite (R.A.)	Glen Harris, Rum	Allivalite	88 91	Optically (universal stage)	3 days at 1350° C.	3 days at 1400° C.	—	D	D–A Many type (c) reflections visible in S. 20 patterns have now disappeared, only the strongest are barely visible. Elongation and diffuse-	A bA Type (c) reflections now disappeared completely. Type (b) reflections very weak.	–

TABLE I (*cont.*)

Bytownite-anorthite (R.E.)	Glen Harris, Rum	Allivalite	88–91	Optically (universal stage)	3 days at 1100° C.	—	—	D	D Same as untreated.	—	—
Bytownite-anorthite (R.G.)	,,	,,	,,	,,	3 days at 900° C.	—	—	D	D Same as untreated.	—	—
Bytownite-anorthite (R.I.)	,,	,,	,,	,,	3 days at 800° C.	—	—	D	D Same as untreated.	—	—
Bytownite (S.2)	Stillwater, Montana	Gabbro	86	Chemical analysis	3 days at 1300° C.	—	—	D	D Same as untreated.	—	—
Bytownite (L.1)	St. Louis Co., Minnesota. (B.M. 1921,33)	Anorthosite	~80	Optically	3 days at 900° C.	3 days at 1250° C.	3 days at 1350° C.	A	A Same as untreated.	A–bA Type (b) reflections less intense relative to main reflections. They are still sharp.	bA Type (b) reflections almost completely disappeared. The strongest, barely visible, are still sharp.
Bytownite (C.B.2)	Crystal Bay, Minnesota	,,	70·1	Chemical analysis	3 days at 1350° C.	—	—	A	bA	—	—

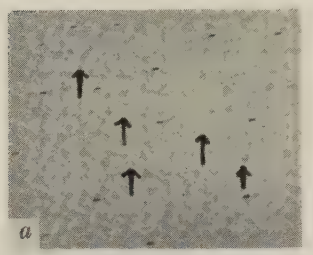
S Pattern
Type (a), reflections present, sharp
Type (b), reflections present, sharp
Type (c), reflections present, sharp
Type (d), reflections present, sharp

D Pattern
Type (a), reflections present, sharp
Type (b), reflections present, sharp
Type (c), reflections present, diffuse
Type (d), reflections absent (?)

A Pattern
Type (a), reflections present, sharp
Type (b), reflections present, sharp
Type (c), reflections absent
Type (d), reflections absent

bA Pattern
Type (a), reflections present, sharp
Type (b), reflections absent
Type (c), reflections absent
Type (d), reflections absent

synthetic anorthite (S.20) and for the specimen (F.5) (see also Laves and Goldsmith, 1951) can take place. No change is found, which supports the suggestion that the S pattern can never be obtained from bytownites. It seems that the increasing albite content lowers the temperature below which the primitive anorthite structure is stable, so that with more than about 10 % Ab the type (c) reflections are always diffuse. The heating of the specimen G.C. suggests that the 'annealing temperature' for the production of sharp (c) reflections is lowered by the increased albite content. Even if this 'annealing temperature' for the Rum material is as high as 500–600° C. it is unlikely that a primitive structure can be formed, since any transition at such low temperatures would proceed very slowly.



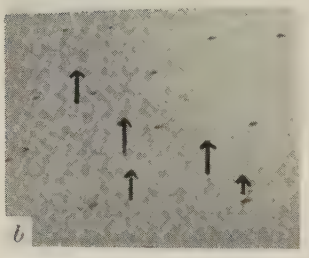


Fig. 1 (a). Section of a zero-layer Weissenberg photograph of untreated bytownite L.1. Some type (b) reflections marked. a-axis oscillation, Cu-$K\alpha$ radiation.

Fig. 1 (b). The same section of a zero-layer Weissenberg photograph of bytownite L.1. after three days at 1350° C. Type (b) reflections marked are barely visible. a-axis oscillation, Cu-$K\alpha$ radiation.

The specimen bytownite L.1 shows the A type pattern in the untreated condition. As the temperature is increased above 1100° C. type (b) reflections begin to fade in intensity with respect to the principal reflections, until at 1350° C. hardly any type (b) reflections remain (fig. 1), i.e. there is a change A → bA. Specimen C.B.2 shows a similar change after being heated at 1350° C. when no type (b) reflections remain. The type (b) reflections do not appear to smear out; even when they are only just visible they seem to be quite sharp. No changes in the intensities of type (b) reflections have been obvious when pure or almost pure anorthites have been heated, although the effect of prolonged heating at very high temperatures is not known. The existence of type (b) reflections for synthetic anorthite suggests that their removal is not possible for pure anorthite. A schematic representation of these structural changes is given in fig. 2.

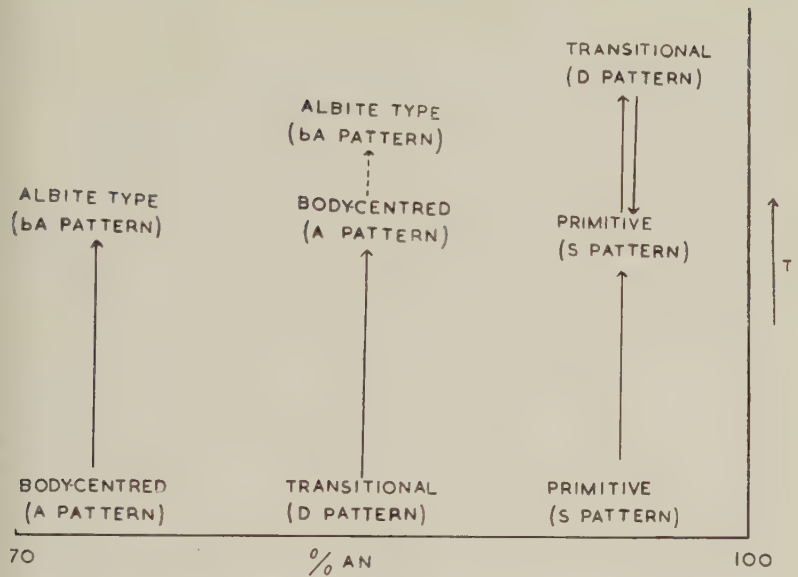


FIG. 2. Schematic representation of structural changes occurring for lime-rich plagioclase felspars.

DISCUSSION.

(*a*) *Thermal history and other observations.* The pattern of the changes which occur when lime-rich felspars are heated is now quite clear, although no detailed information about the temperatures and rates of transformation is available. It has been suggested that the transformations between the high- and low-temperature forms in felspars are order-disorder effects (Buerger, 1948; Laves, 1952). This suggestion is in agreement with the general nature of the changes observed. With such changes, intermediate stages of transition can exist quite stably as has been shown here for several specimens. In natural materials, the final state of the felspar depends, not only on the temperature of the initial crystallization, but also on any subsequent thermal changes.

The significance of intermediate states of transition has not been fully appreciated in the past, particularly by optical workers, who have drawn up determinative optical curves for two series, one for the high-temperature forms and another for the low-temperature forms.[1] It must

[1] The use of the terms 'high'- and 'low'-temperature forms which is common practice is unfortunate; it follows from the discussion above that they are not necessarily the most suitable for the description of the final state of the felspar, e.g.

be realized that these are only two limiting states, and that by the very nature of the inversion, felspars in intermediate states can exist which presumably have intermediate optical and other properties. While this would not be important for the determinative work for the lime-rich felspars considered here, there is little doubt that inversions of this kind exist over the whole of the plagioclase system: the determination of composition for less basic plagioclases by any method other than chemical analysis is complicated by the existence of these intermediate states. Probably the most satisfactory method of composition determination for small fragments such as those used in single-crystal work is by measurement of the refractive index of the fused specimen.

Reynolds (1952) in a critical examination of previous optical data states that 'in the range An_{70} to An_{100}, the question still remains whether two series do in fact exist'. From this work there is little doubt that structurally there is a difference between the high- and low-temperature felspars in this composition range, though the detection of this difference optically may be difficult.

Another important feature revealed by these experiments is the existence in this region of the bA pattern at high temperatures: when the type (b) reflections fade and disappear (types (c) and (d) already having disappeared), the 14 A. *c*-axis characteristic of the anorthite-type structure is halved, and the cell dimensions become similar to those of albite. The existence of a structure giving rise to the bA pattern at high temperatures has been demonstrated for specimens at least up to 80 % An and it seems probable that it persists up to about 90 % An. Some authors have noted that the weak pairs of subsidiary reflections appearing on photographs about the *c*-axis of the intermediate felspars ($\sim$ 30-70 % An) can be further reduced in intensity by heat-treatment (Sörum, 1951) and do not exist for some natural specimens (Cole, Sörum, and Taylor, 1951: Donnay, 1952). In the course of investigations on these materials to be described later, the author has found that all the intermediate plagioclase felspars examined can be homogenized by the appropriate heat-treatment to give a simple homogeneous structure with cell dimensions similar to those of albite. Further, once this homogenization has occurred, it seems very unlikely that any reverse transformation to the normal intermediate felspar structure can be carried out in the laboratory by simple annealing treatments for long periods: all such

a 'low-temperature' felspar may have been at a high temperature but have cooled relatively slowly. The final condition of a particular specimen depends, not only on the temperature which it has reached, but also on the rate of cooling relative to the rate of the high–low transformation.

treatments so far carried out have left the diffraction pattern from the homogenized specimen unchanged.

The existence of the albite structure for plagioclases containing up to 80–90 % An is some confirmation that a complete range of solid solution exists from albite to anorthite at high temperature as suggested by the early thermal work (Bowen, 1913). The discrepancy between previous X-ray work and the thermal work which has been noted by Buerger (1948) and Tuttle and Bowen (1950) arose because the X-ray work was carried out in the main on low-temperature minerals. Buerger suggested that albite and anorthite have a common, disordered, high-temperature form. Unfortunately the region of solid solution does not appear to extend quite as far as pure anorthite, for synthetic anorthite has a well-defined 14 A. *c*-axis. It is possible that a non-quenchable inversion exists for the very basic plagioclases: this point is under examination.

Powder data obtained by Goodyear and Duffin (1954) for a series of synthetic plagioclases show a discontinuity in the region 70–80 % An; this may represent the limit of the region of solid solution, although the present single-crystal work suggests that the region of solid solution may be extended to more anorthite-rich specimens. The same authors, when plotting powder data for natural plagioclases, find two discontinuities, one at about 30 % An, and the other at about 70 % An, as expected from the earlier single crystal work.

(*b*) *Structural interpretation.*—Previous work (Laves and Goldsmith, 1951: Gay and Taylor, 1953) has suggested that the structural changes occurring when pure anorthite is heated are associated with the Ca ions; the Si–Al distribution remains fixed and it is an ordered arrangement. The effect of introducing albite is to promote the changes associated with the Ca ions only: the 14 A. *c*-axis of the anorthite-type structure persists by virtue of the Si–Al ordered arrangement. The present experiments show that at least up to 80–90 % An, the Si–Al arrangement can be disordered by heat-treatment.

It seems likely that the changes associated with the Ca ions are reversible.[1] This is reasonable since the changes are small; they may only be associated with the movement of Ca ions within their interstices in the structure. The changes associated with the redistribution of Si and Al in the tetrahedral framework are necessarily more severe, and, as

[1] Certainly the transformation S → D is reversible. The transformation D → A has not yet been shown experimentally to be possible, although it seems likely; using material showing a D pattern initially, the correct heating conditions to complete the change to the A pattern without affecting the type (b) reflections have not yet been found.

might be expected, it has not been possible to reverse this process in laboratory times.

From the photographic evidence, it appears that the structural changes associated with the Si Al distribution and the Ca ions are essentially of the same kind but differing in degree. Both are continuous in character, but whereas the suggested order–disorder relations of the Si Al arrangement change the type (b) reflections without making them diffuse, the type (c) reflections which are thought to be governed by the Ca ions do become diffuse. Further, it also seems likely that the two structural changes are to some extent interdependent. There appear to be two definite stages in the transition of the anorthite-type structure to one which is akin to albite, for in experiments so far carried out type (b) reflections have shown no change, whilst types (c) and (d) reflections are still present, i.e. the process of change is: primitive anorthite (via transitional structure) → body-centred anorthite → albite-type structure. Thus the Si–Al disordering cannot take place until the changes associated with the cations are complete. The significance of this is not clear, and, together with other structural problems, must await the completion of the accurate structural analyses being carried out.

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Determination of the composition of natural nephelines by an X-ray method.

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Introduction.

In the course of the investigation of the nepheline kalsilite system by Tuttle and Smith an X-ray method for determining the $KAlSiO_4$ content of synthetic nephelines of composition $(Na,K)AlSiO_4$ has been developed. This method is rapid and sensitive to about 1 % in composition; details will be given in a later publication.

Natural nephelines usually do not have the ideal composition $(K,Na)AlSiO_4$, for they often contain excess silica and certain substituted atoms like Ca and Fe. We have, however, used this X-ray method on natural nephelines to see whether it is also applicable to them. If the method proved satisfactory, information on the chemical composition of natural nephelines could be rapidly obtained.

Method and accuracy of measurement.

The nepheline is mixed with pure silicon powder and ground until homogeneous. A small amount is then smeared on a glass slide with a weak solution of Duco cement in acetone. The resultant smear should be thin so that the X-ray reflections are sharp (if the smear is not quite opaque it is of the right thickness). The slide is mounted on a Geiger-counter focusing spectrometer and a record is made from $2\theta_{Cu} = 30°$ to $2\theta_{Cu} = 26{\cdot}5°$ on the scale of one inch per degree of 2θ. The (20·2) and (21·0) nepheline peaks occur near 29·5° and 27·0°, respectively, with the Si line at 28·465°. The positions of the nepheline lines may be corrected by measuring the position of the Si line, for the geometrical errors of the spectrometer are equal for adjacent reflections.

It is mechanically possible to measure the position of each reflection

to an accuracy of 0·01′ in 2θ. There is, however, one difficulty in measuring the lines, for at these angles the α_1 and α_2 components are only partially resolved, giving a slightly asymmetric peak. If all the peaks have the same sharpness and are measured in the same way, no additional error occurs. However, if the peaks have different sharpness (perhaps through zoning of the nephelines) it is possible to get an error unless the centre of gravity of the peak is measured each time. It is advisable, therefore, to measure the centre of gravity or to measure the centre of the peak at a height of one-half. The top of the peak should not be measured. It is probable that this error will not exceed 0·005° in 2θ, if the correct procedure is used.

We have taken four or six records (four by Smith and six by Sahama) for each sample in order to improve the accuracy. Between each record we have moved the slide a little. The mean of the four or six measurements of each reflection should be accurate to about 0·005° in 2θ. The calibration error of the silicon peak is 0·005° and must be added to the error of the nepheline peak, giving a combined random error of about 0·007° ($\sqrt{2}\times 0{\cdot}005$) in the absolute position 2θ of a nepheline reflection.

Independent measurements were made by us on 13 of the samples (table I). The root-mean-square difference between our measurements of

TABLE I. Comparison of independent measurements of 2θ.

Sample.	$2\theta_{(21\cdot0)}$ Sahama.	$2\theta_{(21\cdot0)}$ Smith.	$2\theta_{(20\cdot2)}$ Sahama.	$2\theta_{(20\cdot2)}$ Smith.	Mean $2\theta_{(21\cdot0)}$.	Mean $2\theta_{(20\cdot2)}$.
FEAE 49 ...	27·135°	27·120°	29·550°	29·545°	27·127°	29·547°
FEAE 86 ...	27·015	27·010	29·435	29·435	27·012	29·435
FEAE 87 ...	27·065	27·070	29·510	29·480	27·067	29·495
FEAE 88 ...	27·065	27·040	29·500	29·505	27·052	29·502
FEAE 89 ...	27·060	27·075	29·495	29·480	27·067	29·487
FEAE 90 ...	27·215	27·220	29·635	29·635	27·217	29·635
FEAE 92 ...	27·050	27·065	29·475	29·480	27·057	29·477
FEAE 93 ...	26·990	26·990	29·415	29·425	26·990	29·420
FEAE 170	27·265	27·265	29·700	29·680	27·265	29·690
FEAE 198	27·275	27·270	29·695	29·695	27·272	29·695
C 5549 ...	27·190	27·190	29·605	29·600	27·190	29·602
C 5550 ...	27·135	27·120	29·545	29·555	27·127	29·550
C 9956 ...	26·970	26·965	29·400	29·395	26·967	29·397

2θ (Sahama) is the mean of 6 measurements by Sahama
2θ (Smith) is the mean of 4 measurements by Smith
} to nearest 0·005° in 2θ.

Means to nearest 0·0025° in 2θ.

the 26 values of 2θ is 0·011 ($\sqrt{2}\times 0{\cdot}0078$) in 2θ, in good agreement with the estimated random error. There is a mean difference of 0·003° in 2θ,

but this may be caused by chance, for the error of the mean of 26 differences of standard deviation 0·011 is 0·002 (0·011/$\sqrt{26}$).

TABLE II. Composition and 2θ values of synthetic nephelines.

Composition		2θ	2θ
$NaAlSiO_4$.	$KAlSiO_4$.	(21·0).	(20·2).
40·0 %	60·0 %	26·760°	29·235°
45·1	54·9	26·820	29·280
50·2	49·8	26·875	29·350
52·7	47·3	26·910	29·370
55·2	44·8	26·945	29·380
60·1	39·9	27·005	29·450
62·5	37·5	27·040	29·480
65·0	35·0	27·085	29·530
69·8	30·2	27·140	29·560
73·2	26·8	27·180	29·600
76·9	23·1	27·215	29·635
81·6	18·4	27·245	29·670
90·9	9·1	27·295	29·730

The measurements by Smith of the synthetic nephelines are listed in table II and fig. 1. Each set of 2θ values may be represented by two straight lines which meet near 75 % $NaAlSiO_4$.[1] For nephelines more potash-rich than $Na_{75}K_{25}$ an error of 0·01° in 2θ corresponds to a difference in composition of 0·8 % and 0·9 % for the (21·0) and (20·2) lines, respectively. For compositions less potash-rich than $Na_{75}K_{25}$, the corresponding values are 1·8 % and 1·5 %, giving a lower sensitivity in this region.

MEASUREMENTS OF THE NATURAL NEPHELINES.

The simplest way of comparing the data for the natural and synthetic crystals is to use the ratio K/(K+Na+Ca),[2] for Ca and Na ions have the same size. The measurements of 2θ and the values of K/(K+Na+Ca) for the natural nephelines are given in table III and plotted in fig. 1. The chemical analyses are listed in table IV, and the ratio K/(K+Na+Ca) was determined directly from the oxides.

It will be seen from fig. 1 that there is good agreement between the data for the natural and synthetic nephelines. The maximum deviations are about 4 % in K/(K+Na+Ca) and the average deviation is about 2 %. However, almost all the points for the natural nephelines are

[1] The breaks at 75 % $NaAlSiO_4$ correspond to the composition $Na_3KSi_4Al_4O_{16}$, which is the ideal formula of nepheline (M. J. Buerger, G. E. Klein, and G. Hamburger, Amer. Min., 1947, vol. 32, p. 197). All compositions in the text are given as atomic %.

[2] Ca = 0 for the synthetic crystals.

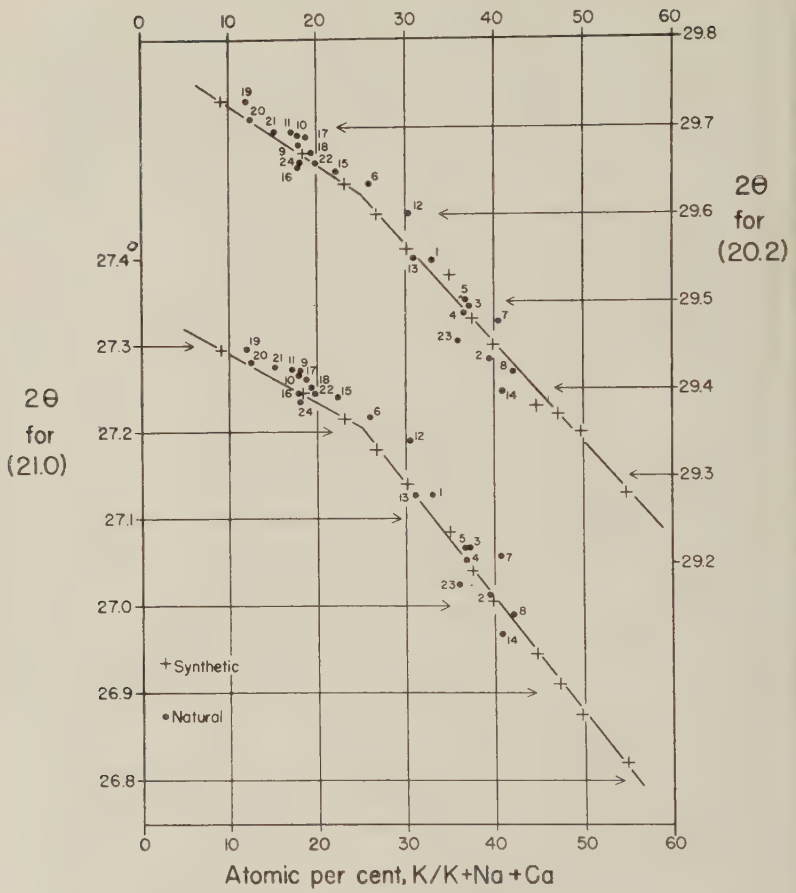

FIG. 1. The variation of $2\theta(21{\cdot}0)$ and $2\theta(20{\cdot}2)$ with K/(K + Na + Ca). The data are given in numerical form in tables II and III. The points for the natural nephelines may be identified by the numbers which correspond to those in column 1 of table III. The curves give the least-squares solutions for the data on the synthetic crystals and their equations are given in the text.

displaced from the curves for the synthetic crystals in the direction of higher K content.

These deviations may be explained by the following possibilities: (*a*) Errors in the composition of the synthetic nephelines. Before growth of the nephelines, the weighed constituents were fused to a glass, during which process some alkali may have been lost. This loss is probably small and, as will be shown later, examination of the natural nephelines

TABLE III. X-ray measurements and chemical compositions of natural nephelines.

	Specimen.	100 K/(K + Na + Ca).	100 K/T.	100 (Na + Ca)/T.	Vacant alkali sites.	Excess Si.	2θ (21·0).	2θ (20·2).	Observer.	Deviation in 2θ (21·0).	Deviation in 2θ (20·2).	Deviation in 2θ Mean.
1.	FEAE 49	33·0	29·0	59·0	12·0 %	0·5 %	27·127°	29·547°	AH	+0·025°	+0·015°	+0·020°
2.	FEAE 86	39·5	37·5	57·3	5·2	0·3	27·012	29·435	AH	−0·005	0·025	−0·015
3.	FEAE 87	37·2	35·2	59·3	5·5	0·7	27·067	29·495	AH	+0·020	+0·010	+0·015
4.	FEAE 88	36·8	34·9	60·0	5·1	0·1	27·052	29·502	AH	+0·000	+0·012	+0·005
5.	FEAE 89	36·6	34·6	59·8	5·6	0·4	27·067	29·487	AH	+0·012	−0·005	+0·005
6.	FEAE 90	25·9	24·3	69·5	6·2	5·5	27·217	29·635	AH	+0·025	+0·022	+0·025
7.	FEAE 92	40·6	38·6	56·4	5·0	2·7	27·057	29·477	AH	+0·055	+0·030	+0·042
8.	FEAE 93	42·1	39·7	54·5	5·8	1·9	26·990	29·420	AH	+0·007	−0·010	+0·000
9.	FEAE 134	18·0	15·9	72·5	11·6	12·7	27·270	29·680	A	+0·025	+0·010	+0·017
10.	FEAE 170	17·9	16·0	73·5	10·5	14·7	27·265	29·690	AH	+0·020	+0·017	+0·020
11.	FEAE 198	17·1	15·5	75·1	9·4	13·4	27·272	29·695	AH	+0·022	+0·017	+0·020
12.	C 5549	30·4	—	—	—	—	27·190	29·602	AH	—	—	—
13.	C 5550	31·0	31·3	69·8	1·1	4·8	27·127	29·550	AH	+0·000	−0·005	+0·000
14.	C 9956	40·8	38·7	56·1	5·2	0·3	26·967	29·397	AH	0·032	−0·047	0·040
15.	E 2	22·3	22·1	76·7	1·2	4·9	27·240	29·650	H	+0·020	+0·007	+0·012
16.	238	17·9	16·3	74·6	9·1	0·7	27·245	29·655	H	+0·000	−0·017	−0·007
17.	273	18·8	17·8	77·1	5·1	7·0	27·260	29·690	H	+0·020	+0·022	+0·022
18.	276	19·4	18·6	77·4	4·0	7·8	27·250	29·670	H	+0·010	+0·010	+0·010
19.	63197	12·0	11·3	82·5	6·2	16·9	27·295	29·730	H	+0·015	+0·017	+0·015
20.	34475	12·5	11·7	82·5	5·8	8·0	27·280	29·710	A	+0·002	+0·000	+0·000
21.	34480	15·2	14·5	80·8	4·7	8·2	27·275	29·695	A	+0·015	+0·005	+0·010
22.	Iivaara	19·8	18·6	75·6	5·8	−0·2	27·245	29·660	A	+0·010	+0·000	+0·005
23.	R 118	36·0	35·0	62·2	2·8	0·8	27·025	29·455	H	−0·037	0·045	−0·040
24.	Gooderham	18·1	16·6	75·1	8·3	8·4	27·235	29·660	H	−0·010	−0·010	−0·010
				Average	6·0	4·9						

$T = \frac{1}{2}(Si + Al + Fe + Mn + Mg + Ti)$.
Excess $Si = Si - (Al + Fe + Mn + Mg + Ti)/Al + Fe + Mn + Mg + Ti$.
Observer: A denotes Sahama and H denotes Smith.

TABLE IV. Chemical analyses of the natural nephelines.

Specimen	FEAE 49	FEAE 86	FEAE 87	FEAE 88	FEAE 89	FEAE 90	FEAE 92	FEAE 93
SiO_2	41·30	40·81	41·01	40·89	41·01	42·12	41·14	41·05
TiO_2	0·13	0·06	0·09	0·07	0·07	0·07	0·06	0·07
Al_2O_3	33·07	33·39	33·59	33·54	33·52	32·96	32·89	33·27
Fe_2O_3	1·77	1·05	0·89	1·03	1·08	0·65	1·02	0·84
FeO	0·28	0·28	0·18	0·18	0·18	0·52	0·25	0·18
MnO	0·01	0·01	0·01	0·01	0·00	0·01	0·02	0·01
MgO	0·30	0·16	0·17	0·22	0·22	0·08	0·18	0·16
CaO	0·51	0·88	0·78	0·89	0·91	0·91	0·87	0·90
Na_2O	12·25	11·57	12·08	12·17	12·14	14·21	11·35	10·95
K_2O	9·36	11·98	11·28	11·18	11·09	7·83	12·29	12·65
CO_2	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
H_2O^+	0·87	0·12	0·12	0·07	0·09	0·47	0·13	0·08
H_2O^-	0·10	0·00	0·00	0·00	0·00	0·02	0·00	0·00
Total	99·95	100·31	100·20	100·25	100·31	99·85	100·20	100·16
Reference	1	2	2	2	2	1	2	2

Specimen	FEAE 134	FEAE 170	FEAE 198	C 5549	C 5550	C 9956	E 2	238
SiO_2	45·04	44·47	44·26	—	40·78	40·20	42·23	41·98
TiO_2	0·02	0·04	0·05	—	0·07	0·05	—	0·00
Al_2O_3	33·25	32·10	32·25	—	30·95	32·51	34·08	35·09
Fe_2O_3	0·55	0·94	0·97	—	2·41	1·82	0·12	0·16
FeO	0·28	0·18	0·29	—	0·57	0·57	—	—
MnO	0·01	0·01	0·01	—	n.d.	n.d.	—	—
MgO	0·07	0·03	0·01	—	0·07	0·10	0·00	0·14
CaO	0·00	0·47	0·32	—	0·78	1·44	0·15	1·74
Na_2O	15·89	15·54	15·96	13·23	13·93	10·86	16·21	15·15
K_2O	5·30	5·23	5·06	8·78	9·78	12·22	7·12	5·35
CO_2	n.d.	0·00	0·00	—	n.d.	n.d.	—	—
H_2O^+	0·08	1·11	0·64	—	0·32	0·00	—	0·00
H_2O^-	0·00	0·04	0·00	—	0·00	0·00	0·03	0·29
Total	100·49	100·16	99·82	...	99·66	99·77	99·94	99·90
Reference	3	1	1	4	4	4	5	6

Specimen	273	276	63197	34475	34480	Iivaara	R 118	Gooderham
SiO_2	43·29	43·33	44·65	43·42	43·24	41·48	40·74	43·60
TiO_2	—	0·00	0·00	0·00	0·00	0·00	0·11	trace
Al_2O_3	34·25	34·00	32·03	33·92	33·56	34·12	33·39	34·02
Fe_2O_3	0·13	0·18	0·59	0·14	0·47	1·26	0·83	0·10
FeO	—	—	—	n.d.	n.d.	0·29	—	—
MnO	—	—	—	0·00	0·00	0·00	—	trace
MgO	0·00	0·00	0·00	0·08	0·05	0·12	0·25	0·04
CaO	0·51	0·26	0·71	1·37	0·77	trace	0·91	0·75
Na_2O	16·43	16·54	17·25	17·05	16·88	16·20	12·53	15·82
K_2O	5·86	6·10	3·66	3·85	4·71	6·06	11·13	5·47
CO_2	0·08*	—	—	—	—	—	—	—
H_2O^+	—	—	0·96	—	—	0·17	0·23	0·16
H_2O^-	0·02	0·03	0·21	0·11	0·07	0·00	0·06	—
Total	100·57	100·44	100·06	99·94	99·75	99·70	100·18	99·97†
Reference	6	6	7	7	7	8	9	10

* Calcite.

† Including Li_2O 0·01.

1. To be published by Sahama. FEAE 49, collected by the Finnish East African Expedition, Nyamunnka crater, Katwe-Kikorongo field, Uganda; FEAE 90, 0·5 km. E. of Mt. Goma, Congo; FEAE 170, Ol Esakut, Kenya; FEAE 198, 6·0 miles from Lumbwa on the Lumbwa–Kericho road, Kenya. Analyst, P. Ojanperä.
2. Sahama (Th. G.), Ann. Acad. Sci. Fennicae, 1953, ser. A, no. 35. [M.A. **12**–372.] Analyst, P. Ojanperä.
3. To be published by Kai Hytönen. From natrolite-sodalite-tinguaite, Toror Hills, Karamoja, Uganda. Analyst, H. B. Wiik.
4. Sahama (Th. G.), Amer. Journ. Sci., 1952, Bowen vol., p. 457. [M.A. **12**–146.] Analyst, H. B. Wiik.
5. Tilley (C. E.), Geol. Mag., 1953, vol. 90, p. 148. [M.A. **12**–268.] Analyst, J. H. Scoon.
6. To be published by C. E. Tilley. 238, York River, E. of Bancroft, Ontario; 273, ¾ mile E. of Bancroft, Ontario; 273, Temo, Nyasaland. Analyst, J. H. Scoon.
7. Tilley (C. E.), Amer. Journ. Sci., 1954, vol. 252, p. 65. [M.A. **12**–371.] Anal. J. H. Scoon.
8. To be published by Mauno Lehijärvi. From ijolite, Iivaara, Kuusamo, Finland. Analyst, M. Lehijärvi.
9. Bowen (N. L.) and Ellestad (R. B.), Amer. Min., 1936, vol. 21, p. 363. [M.A. **7**–29.] Analyst, R. B. Ellestad.
10. Yoder (H. S.) and Weir (C. E.), Amer. Journ. Sci., 1951, vol. 249, p. 683. [M.A. **11**–491.] Analyst, E. G. Zies.

suggests that the lattice parameters are almost independent of loss of alkali. (*b*) The structure of synthetic nephelines may differ slightly from that of natural nepheline, thus giving different lattice parameters. This difference might arise from order-disorder between the ions in tetrahedral positions, such as is proposed for the high- and low-felspar series. (*c*) The nepheline might contain some kalsilite as an impurity, which would be difficult to detect optically. However, 1 % of kalsilite can be detected in X-ray patterns, because it has a strong reflection at $2\theta_{Cu} = 28{\cdot}7^{\circ}$. No kalsilite was detected in the nepheline samples, showing that the error in the chemical composition is not more than 1 %. (*d*) Errors in the chemical analysis of the natural nephelines. These may be estimated from the paper by Fairbairn and Schairer (1952) which described tests on the chemical analyses of a glass of known composition. (*e*) The deviation of the chemical formula of the natural nephelines from $(K,Na)AlSiO_4$.

The compositions of the natural nephelines studied here deviate considerably from the ideal formula and allow consideration of the effect of these deviations on the X-ray reflection angles. All of the natural nephelines contain small amounts of Ca, Mg, Fe, Mn, and Ti which replace the dominant cations. In addition, all but one of the chemical analyses show a deficiency in the sum of the alkali ions in comparison with the number of ions in tetrahedral positions, and all but two of the analyses show an excess of silica. In view of these complex factors the problem of interpreting the data must be simplified.

The chemical analyses were converted from weight % of oxide to number of atoms (H_2O^+ was neglected because of the uncertainty of its determination and of its role). It is well known that Na and Ca have very similar ionic sizes, so they were added together. The K ion is much larger,

and this, of course, is the chief reason for the variation of X-ray spacing in the nephelines. The Fe″, Fe‴, Mn, Mg, and Ti ions were added to the Al ions because they have approximately the same size and the amounts of Fe, &c., were small anyway.

The sites for tetrahedra in the structure should be fully occupied, for the tetrahedrally bonded ions are tightly bound to the oxygen atoms, and a vacancy would lead to a large structural imperfection. A vacancy in an alkali site, however, would give a smaller imperfection since the alkali ions are less strongly bonded. The total number of sites for alkali ions may be obtained by dividing Si+(Al, &c.) by 2. In the ideal nepheline formulae, Si = Al; however, in the 23 analyses considered here, the excess of Si [taken as Si−(Al, &c.)/(Al, &c.)] varied from −0·3 to +16·9 % with an average excess of 4·9 %. A test of the accuracy of chemical analyses by 14 analysts (Fairbairn and Schairer, 1952)[1] showed that there was a tendency to underestimate SiO_2 by $\sim 0{\cdot}5$ % and to correspondingly overestimate Al_2O_3. This suggests that the excess Si found in these 23 analyses should be an underestimate and *not* an overestimate, but the total of Si+Al should be correct. It should be noted that all the tetrahedral sites can be filled even when Si is in excess, for Si ions can occupy Al positions. Comparison of the number of alkali ions with the number of sites shows that there is a deficiency varying from −1·1 to +12·0 % with an average deficiency of 6·0 %.

This deficiency cannot be explained by analytical error, for the data of Fairbairn and Schairer (1952) showed no appreciable systematic bias in the determination of total alkali and total (Si+Al). Bannister[2] also found that natural nephelines usually have excess Si and a deficiency of alkali.

From the data of Fairbairn and Schairer[1] it is possible to estimate the analytical precision of the ratio K/(K+Na). This ratio was calculated for the 14 sets of K_2O and Na_2O. The root-mean-square error is 1·75 %; however, if one analysis is omitted the error is reduced to 0·75 %. The mean analytical value is 53·7 % compared with the value 54·3 % calculated from the weights of the pure constituents used in the test material. It is likely, therefore, that the chemical analyses given in this paper will give values of K/(K+Na) which have random errors of 1 to 2 % and a systematic bias of $\sim 0{\cdot}5$ %.

The effects of alkali deficiency and of excess Si were studied by

[1] H. W. Fairbairn and J. F. Schairer, Amer. Min., 1952, vol. 37, p. 744. [M.A. 12-33.]

[2] F. A. Bannister, Min. Mag., 1931, vol. 22, p. 569.

examining the deviations of the natural nephelines from the curves of 2θ for the synthetic crystals. The quantity $\Delta = 2\theta_{obs} - 2\theta_{calc}$ was determined. ($2\theta_{obs}$ is the measured value; $2\theta_{calc}$ is the 2θ value for a synthetic crystal of composition K/(K + Na) equal to the value K/(K + Na + Ca) calculated from the chemical analysis of the natural nepheline.) It was

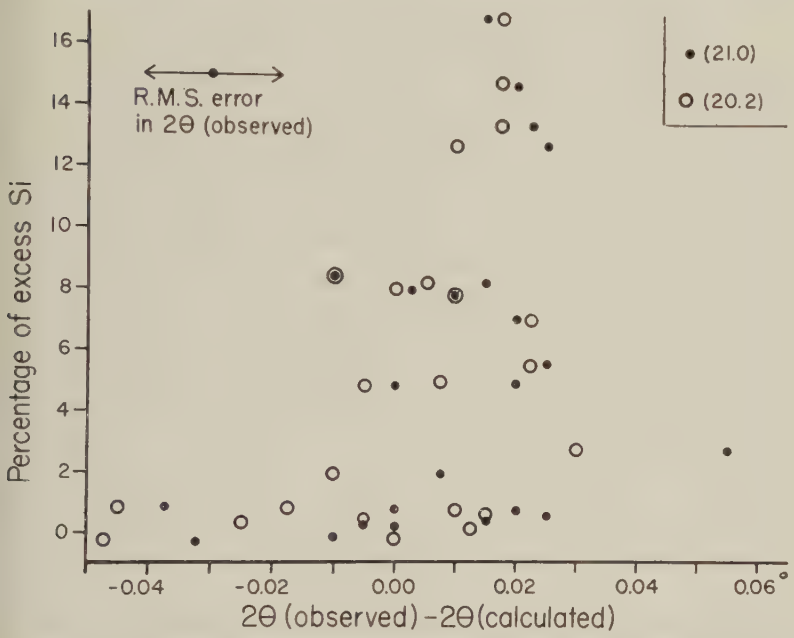

FIG. 2. The relation between excess silica and $2\theta_{obs} - 2\theta_{calc}$ for the natural nephelines. $2\theta_{obs}$ is the measured value whereas $2\theta_{calc}$ is the 2θ value of the synthetic nepheline whose K/(K + Na) ratio is equal to the K/(K + Na + Ca) ratio of the natural nepheline. The data are given in table III.

found that the values of Δ were, on the average, independent of the deficiency of alkali. This was rather surprising for it was expected that a vacant site would act as though it were occupied by a small ion like Na and thus reduce the value of K/(K + Na + Ca). Fig. 2 shows the relation between Δ and excess Si. The values of Δ for the (21·0) and (20·2) reflections are given in table III. It will be seen that the correlation between Δ (21·0) and Δ (20·2) is high; however, Δ (21·0) on the average is 0·004° greater than Δ (20·2). Examination of fig. 2 shows that there are large random deviations which are considerably larger than the experimental error in the 2θ measurements, and it is thus difficult to determine

whether Δ is a function of excess Si. There is a suggestion that both Δ (21·0) and Δ (20·2) increase by about 0·01° in 2θ for a 10 % increase in the excess Si, but a statistical analysis shows that there is a 5 % probability that it is caused merely by random fluctuations. The values of Δ for those nephelines which have only small amounts of excess Si have an average value close to zero and there is, therefore, no reason to suppose that natural nephelines which contain no excess Si have different lattice parameters from the pure synthetic nephelines. An increase in Δ corresponds to a decrease in the lattice parameters of the natural nephelines. As the ionic radius of Si is less than that of Al, Δ would be expected to increase with increasing excess Si, as suggested by the present data.

The natural nephelines fit quite well with the synthetic nephelines and there is no evidence for any appreciable systematic bias (other than the possible effect of excess silica). The random error of measurement of K/(K+Na+Ca) is about 1 % for both the X-ray and chemical analysis methods. The largest observed deviation between the values of K (K+Na+Ca) for the two methods is 3·7 %. The curves for the synthetic crystals can therefore be used for the determination of K (K+Na+Ca) by the X-ray method. If the natural nepheline contains 10 % or more excess silica it is possible that the measured values of 2θ will be about 0·01° too high and the X-ray value for K (K+Na+Ca) will correspondingly be 1 to 2 % too high.

The following linear equations, calculated by least-square methods, represent the data for the synthetic nephelines:

(21·0) reflection for 100K/(K+Na) from 9 to 25 %:

$$100K/(K+Na) = 61{\cdot}24\text{–}176{\cdot}3\ (2\theta_{Cu}\text{–}27{\cdot}00^{\circ}).$$

(21·0) reflection for 100K/(K+Na) from 25 to 60 %:

$$100K/(K+Na) = 118{\cdot}02\text{–}77{\cdot}26\ (2\theta_{Cu}\text{–}26{\cdot}00^{\circ}).$$

(20·2) reflection for 100K/(K+Na) from 9 to 25 %:

$$100K/(K+Na) = 117{\cdot}35\text{–}148{\cdot}1\ (2\theta_{Cu}\text{–}29{\cdot}00^{\circ}).$$

(20·2) reflection for 100K/(K+Na) from 25 to 60 %:

$$100K/(K+Na) = 79{\cdot}94\text{–}88{\cdot}13\ (2\theta_{Cu}\text{–}29{\cdot}00^{\circ}).$$

It is recommended that these equations be used for the X-ray determination of the K/(K+Na+Ca) ratio for natural nephelines.

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requisite for the work described here. We are also indebted to Professor C. E. Tilley, Drs. N. L. Bowen and H. S. Yoder, Messrs. K. Hytönen and M. Lehijärvi for the supply of specimens, in some cases prior to publication. We are grateful to Drs. Felix Chayes and W. S. MacKenzie for advice on the presentation of the data.

Truscottite.

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[Read June 10, 1954.]

Introduction.

THE mineral truscottite was discovered at the Lebong Donok mine, Benkulen, Sumatra, by Hövig[1] in 1914. He considered it to be a hydrated calcium silicate of composition $CaO.2SiO_2.\frac{1}{2}H_2O$. Later work by Grutterink[2] suggested a different formula, $2(Ca,Mg)O.3SiO_2.2H_2O$, the water content being reduced to 1·3 molecules after drying at 120°. Grutterink noted that the composition, general character, and optical properties indicated a similarity to gyrolite. Flint, McMurdie, and Wells[3] concluded from X-ray powder photographs that the two species were identical, although they detected quartz as an impurity in the truscottite examined. All known specimens of truscottite come from the original locality, and no further investigations have been reported.

The present investigation.

Material.—A specimen (B.M. 1925,1044) was kindly made available by the Trustees of the British Museum. It consisted of aggregates of plates having a pearly lustre: the appearance, and also the optical properties, agreed closely with the earlier descriptions. In parts of the specimen, closely intergrown quartz was detected optically and by X-ray powder photographs. No other minerals were observed, but powder photographs suggested that traces of some additional species, possibly calcite, might be present.

[1] P. Hövig, Jaarboek van het Mijnwezen in Nederlandsch Oost-Indië, Batavia, 1914, vol. 41 (for 1912), p. 202. [Min. Mag. **20**–466.]

[2] J. A. Grutterink, Verh. Geol.-Mijnb. Genootschap Nederland, Geol. Ser., 1925, vol. 8, p. 197. [M.A. **3**–271.]

[3] E. P. Flint, H. F. McMurdie, and L. S. Wells, Journ. Res. Nat. Bur. Standards, U.S.A., 1938, vol. 21, p. 617. [M.A. **7**–283.]

X-Ray single-crystal examination.—X-ray oscillation, rotation, and Weissenberg photographs indicated a hexagonal unit-cell with a 9·72 ± 0·01 and c 18·71 ± 0·03 A., having c perpendicular to the principal cleavage. The c-rotation photograph is shown in fig. 1*a* with that of gyrolite[1] for comparison (fig. 1*b*).

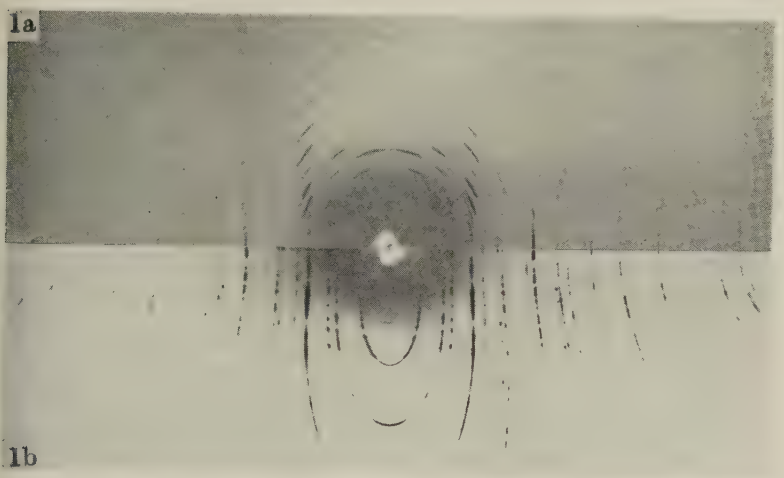

Fig. 1a. X-ray single-crystal photograph of truscottite. Rotation about the c-axis. Cu-$K\alpha$ radiation.

Fig. 1b. Ditto of gyrolite (Mackay and Taylor, 1953).

Two kinds of disorder were observed in all the flakes examined. Firstly, c-rotation photographs (fig. 1a) show considerable angular spread of all reflections, implying that the c-axes of the crystal particles are dispersed by up to 10° in all directions from the mean direction normal to the cleavage. Secondly, Laue photographs, taken with the X-ray beam perpendicular to the cleavage, showed that even the smallest flakes examined were composed of several individuals markedly rotated in the plane of the flake with respect to each other. Because of the disorder, determination of the exact symmetry is difficult. One Laue photograph gave definite indications of trigonal rather than hexagonal symmetry. All oscillation photographs about the c-axis showed slight departures from an equatorial plane of symmetry, but no systematic absences were observed. Certain classes of absences would be obscured by the disorder, but there are certainly no absences among the 000*l*'s

[1] A. L. Mackay and H. F. W. Taylor, Gyrolite. Min. Mag., 1953, vol. 30, pp. 80–91. (Correction, p. 80: for B.M. 1925,1044 read B.M. 93504.)

(fig. 1a) and the lattice is therefore not rhombohedral. $h0hl$ and $h.h.\overline{2h}.l$ reflections are present whether l is even or odd, showing that no c-glide-plane exists. These facts indicate that the Laue symmetry is $\bar{3}$ or $\bar{3}m$, and the diffraction symbol $\bar{3}P-$ or $\bar{3}mP- - -$. The space group could therefore be $P3$, $P\bar{3}$, $P3m1(P31m)$, $P321(P312)$, or $P\bar{3}m1(P\bar{3}1m)$.

X-ray powder examination.—X-ray powder data, obtained using

Table I. X-ray powder data for truscottite (B.M. 1925,1044). (Cu-$K\alpha$ radiation.)

Observed.		Calculated.		Observed.	
d(Å.)	Int.	Indices.	d(Å.)	(dÅ.)	Int.
19	s	0001	18·71	1·469	vw
9·4	s	0002	9·36	1·439	vw
7·65	mw	$10\bar{1}1$	7·65	1·417	vvw
6·30	w	0003	6·24	1·407	w
5·02	vw	$10\bar{1}3$	5·02	1·381	vvw Q
4·65	mw	0004	4·68	1·371	vw Q
4·13	s	$20\bar{2}0$	4·20	1·348	w
3·80	mw	$11\bar{2}3$	3·83	1·316	w
3·71	w	0005	3·74	1·298	vw
3·47	mw	$20\bar{2}3$	3·49	1·266	vvw
3·34	w Q	$(10\bar{1}5)$	(3·42)	1·240	vw
3·14	s	$21\bar{3}1$	3·14	1·215	vvw
—	—	0006	3·12	1·200	vvw Q
3·00	m *	$21\bar{3}2$	3·01	1·181	w
2·83	s	$21\bar{3}3$	2·84	1·175	vvw
2·63	s	$21\bar{3}4$	2·63	1·165	w
2·49	vw	$20\bar{2}6$	2·51	1·055	vw
2·42	w	$21\bar{3}5$	2·42	1·035	w
2·26	w Q	$31\bar{4}2$	2·27		
2·23	w Q	$21\bar{3}6$	2·23		
2·08	w	$31\bar{4}4$	2·09		
2·04	w	$21\bar{3}7$	2·05		
1·921	w	$32\bar{5}0$	1·934		
1·893	vw	$21\bar{3}8$	1·885		
1·836	ms	$41\bar{5}0$	1·835		
1·801	w	$41\bar{5}2$	1·806		
1·762	w	$41\bar{5}3$	1·762		
1·750	mw	$21\bar{3}9$	1·741		
1·717	vvw	$41\bar{5}4$	1·710		
1·690	vvw	$22\bar{4}8$	1·687		
1·652	w	$41\bar{5}5$	1·650		
1·618	vvw	$2.1.\bar{3}.10$	1·616		
1·585	vw	$42\bar{6}0$	1·590		
1·569	vw	$42\bar{6}2$	1·570		
1·557	vw	$21\bar{4}9$	1·553		
1·507	w	$42\bar{6}4$	1·508		

Intensities estimated visually; s strong, m moderate, w weak, v very. Q, line due partly to quartz. *, line due partly to unidentified species (calcite ?). Calculated spacing and indices in parentheses, line probably due almost entirely to quartz. Lines due wholly to quartz are omitted.

cameras of 6 cm. and 19 cm. diameter with Cu-$K\alpha$ radiation, are given in table I. Unlike the gyrolite photograph, all lines in the pattern were sharp. The spacings were indexed by direct comparison with single-crystal photographs: comparison with a *c*-rotation photograph of gyrolite was also useful for determining the *hk* indices. The specimen contained a small proportion of quartz, and traces of a further unidentified impurity, possibly calcite: the lines due to these phases could be distinguished by their rough appearance, and also by the fact that corresponding reflections did not appear on single-crystal photographs.

Chemical analysis and specific gravity. -The results obtained in the present and earlier investigations are given in table II, columns 1–4.

TABLE II. Chemical analyses of truscottite.

		1.	2.	3.	4.	5.		6.	7.
SiO_2	...	62·52	63·94	57·83	58·95	50·23	Si	... 22·9	24
Al_2O_3	...	1·24	2·68	0·95	1·03	2·19	Al	... 0·5	—
Fe_2O_3				0·08	0·03	0·20	Mn	... 0·1	—
MnO	...	—	—	0·25	0·18	—	Mg	.. 0·2	—
MgO	...	—	—	5·33	0·27	0·13	Ca	... 10·7	12
CaO	...	30·20	29·20	26·43	25·54	34·04	Na	... 0·8	—
Na_2O	...	—	—	0·78	1·03	0·14	K	... 0·7	—
K_2O	...	—	—	0·73	1·37		S	... 0·7	—
SO_3	...	—	—	—	2·57	—	C	... 1·2	—
CO_2	...	—	—	—	2·32	0·95	H	... 12·0	12
H_2O+	...	3·85	2·68	4·10	4·61	11·98	O	... 68·9	66
H_2O-				3·41	1·07				
		97·81	98·50	99·89	98·97	99·86			

1. P. Hövig, loc. cit. Analyst, J. E. Clennell.
2. P. Hövig, loc. cit. Analyst, R. T. G. Bayley.
3. J. A. Grutterink, loc. cit. Analyst, J. de Vries; mean of two similar analyses. Also, TiO_2 and F absent; total Fe as Fe_2O_3; $H_2O \pm 120°$ C.
4. New analysis, by F. J. McConnell (Building Research Station, Watford, Hertfordshire), on 450 mg. Also TiO_2 absent; $H_2O \pm 110°$ C.
5. Gyrolite, for comparison; analysis by F. J. McConnell in A. L. Mackay and H. F. W. Taylor, loc. cit.
6. Atomic contents of unit-cell, calculated from column 4 after deduction of $H_2O-110°$.
7. Atomic contents of unit-cell, calculated for $12[CaO.2SiO_2.\frac{1}{2}H_2O]$.

For comparison, an analysis of gyrolite (column 5) is included. The specific gravity of the present material was found by suspension to be 2·48.

Dehydration curve.—A dehydration curve was determined and is given in fig. 2. At temperatures up to 560° C., the partial pressure of water-vapour was maintained at 6 mm. The corresponding curve for gyrolite

(Mackay and Taylor, loc. cit.) is included for comparison; the method employed in both cases is described elsewhere.[1]

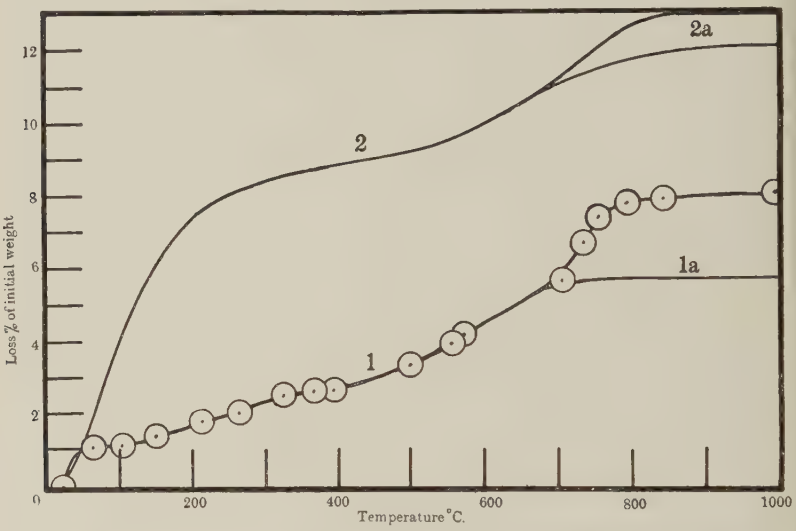

Fig. 2. Dehydration curves: 1, of truscottite; 2, of gyrolite (Mackay and Taylor, 1953); 1a and 2a after correction for CO_2.

X-ray investigation of dehydrated material.—X-ray photographs were taken of single crystals which had been heated to various temperatures for from four to twelve hours. Heating at 110°, 450-500°, or 700° C. caused no detectable change in the pattern. Heating at 770° brought about partial conversion into an unidentified phase giving a weak X-ray pattern with only slight preferred orientation. At 870°, the truscottite pattern disappeared entirely and the unidentified phase alone appeared to be present. After heating at 950 1000°, a strong pattern was again obtained, which indicated the presence of wollastonite (or parawollastonite) with smaller amounts of pseudowollastonite and cristobalite. No preferred orientation was observed. Heating to 1200° gave a pattern indicating predominantly pseudowollastonite.

Discussion.

The relationship of truscottite to gyrolite.—The present results show that truscottite is a distinct species, not identical with gyrolite, although a close relationship exists between the two minerals. Significant differences

[1] H. F. W. Taylor, Journ. Chem. Soc. London, 1953, p. 163. [M.A. **12**-172.]

exist in the unit-cell dimensions and in the composition. Both in truscottite and in gyrolite the unit-cell is hexagonal (or trigonal), and the a-axes of the two minerals are identical; it is therefore probable that truscottite has basically the same (as yet unknown) layer-structure as gyrolite. The c-axes differ, however, being 18·71 A. in truscottite against 132·8 ($6 \times 22{\cdot}13$) A. in gyrolite (Mackay and Taylor, loc. cit.). Rotation photographs about c (figs. 1a and 1b) thus show the same series of row-lines but their layer-lines do not coincide.

Comparison of figs. 1a and 1b shows that all the strong arcs in the truscottite photograph have their centres on groups of strong spots in the gyrolite photograph. Certain points of resemblance in the powder photographs thus also occur, although these cannot be considered identical. The $000l$ reflections of truscottite are strong and weak in bands at much the same θ values as in the case of gyrolite although the indices for regions of corresponding intensity do not coincide.

The above circumstances very strongly indicate that the basic structural units of truscottite and gyrolite are the same. If this is so, and the difference between the minerals resides in the way in which the units are stacked (and also in the possible inclusion of a layer of water molecules in the case of gyrolite), then the continuous transforms of the basic units are identical, but due to the repetition of the pattern at different intervals the transform is sampled in different places. The resultant X-ray patterns are therefore dissimilar in detail, but the general distribution of intensity is much the same in each case.

The composition of truscottite.—The analysis of the present specimen is given in table II, column 4. Together with the unit-cell dimensions already given, this yields the atomic cell contents given in column 6; in making the calculation H_2O-110° was assumed to be uncombined, because the dehydration curve (fig. 2, curve 1) showed that no loss occurs between 65° and 110°. The results are in substantial agreement with the view, expressed in column 7, that the unit-cell contents are $12[CaO.2SiO_2.\frac{1}{2}H_2O]$, with some isomorphous replacement, especially in the case of the calcium. More detailed interpretation of the analysis seems unjustified, in view of uncertainties regarding the role of some of the minor constituents (Al_2O_3, CO_2 and SO_3).

The present results thus support the formula originally proposed by Hövig, rather than the one $(2(Ca,Mg)0.3SiO_2.2H_2O)$ later proposed by Grutterink. A further objection to the latter formula can be made on crystallographic grounds, in that attempts to reconcile it with the unit-cell dimensions and specific gravity indicate non-integral numbers of

molecules in the unit-cell. As shown above, this objection does not apply to Hövig's formula, $CaO.2SiO_2.\frac{1}{2}H_2O$, which yields results compatible with the observed symmetry.

The main discrepancies between Grutterink's analyses (table II column 3) and the present one (column 4) lie in the higher content of MgO and in the absence of values for CO_2 and SO_3. Hövig's analyses (columns 1 and 2), although difficult to interpret, give no indication of MgO. The high content of MgO found by Grutterink was possibly caused by impurity, since he states (loc. cit., p. 198) that the powder taken for analysis was not completely homogeneous.

Although the formula accepted here is not the same as that of gyrolite, it shows a resemblance in that the number of Si atoms in the cell is the same (24) as the number in the layers, 22·13 Å. thick along the *c*-axis, which constitute one-sixth of the unit-cell of gyrolite. This is in accordance with the view that the structures of the two minerals are related.

Behaviour on dehydration.—The dehydration curves (fig. 2) of truscottite and gyrolite both show a break at about 400° C., and if it is assumed that CO_2 is not lost below this temperature, the quantities of water (expressed as $H_2O : SiO_2$ molar ratios) remaining at 400° are approximately the same (1 : 6). The percentage of water lost below 400° is, however, considerably larger in the case of gyrolite. It has been suggested (Mackay and Taylor, loc. cit.) that this water may be present in the form of molecules, and the presence of a larger number of water molecules, and also of additional calcium ions, could account for the expansion of the layer thickness from 18·71 Å. in truscottite to 22·13 Å. in gyrolite.

When gyrolite undergoes complete dehydration at 1000° C. the principal product is oriented pseudowollastonite (Mackay and Taylor, loc. cit.), but truscottite at this temperature yields mainly unoriented wollastonite. In the case of gyrolite, the formation of pseudowollastonite at temperatures at which it was only metastable was assumed to indicate a similarity in structure, and it might therefore have been supposed that truscottite would behave in the same way. That it does not may possibly be due to the fact that pseudowollastonite is much less able to accommodate other atoms in its lattice in place of calcium than is wollastonite, for the extent of such replacement is somewhat greater in truscottite than in gyrolite (table II, columns 4 and 5). After heating gyrolite to 1000° or above, no products other than pseudowollastonite or wollastonite were detected by X-rays, but when truscottite is heated to 1000°, cristobalite can be found among the products. This difference may partly be due to the greater proportion of silica set free in the case

of truscottite, which would make its X-ray pattern more readily discernible in that of the mixture. The silica appears also, however, to be in a more crystalline condition.

The dehydration mechanisms of gyrolite and truscottite evidently differ. In the first case, it appears likely that, with the expulsion of the water and part of the silica, relatively small atomic displacements suffice to convert the structure into that of pseudowollastonite, which is therefore formed although it is unstable under the prevailing conditions. With truscottite, on the other hand, a more drastic rearrangement occurs, giving as the immediate product (at 750–850° C.) an unidentified intermediate phase with very little preferred orientation. At about 900° this loses silica and is converted to wollastonite, which is stable at this temperature. A little pseudowollastonite is apparently formed at 1000°, possibly by the mechanism which operates in the case of gyrolite, but pseudowollastonite is the main product only when the material has been heated to 1200°, under which conditions the normal transition from wollastonite to pseudowollastonite takes place.

Acknowledgements.—We thank the Trustees of the British Museum for the specimen of truscottite, and Mr. F. J. McConnell (Building Research Station, Watford, Hertfordshire) for the chemical analysis. Much of the work was carried out as part of an extra-mural contract for the Building Research Board, and we thank the Director of Building Research for permission to publish this paper.

Zoisite-amphibolite with corundum from Tanganyika.

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(Natural History).

[Taken as read 10 June, 1954.]

Occurrence.

THE most striking rock now described occurs in the Northern Province of Tanganyika Territory, just west of the Great North road, and south of the track from Longido to Engare Naibor. A small group of specimens was collected by Mr. A. G. Clough of Industrial Minerals Ltd., and presented to the British Museum (Natural History) in 1952 (B.M. 1952,133). The outcrops occur in the highly metamorphosed Basement Complex which forms small hills (The Matabatu Mountains) descending, at their margin, by step-faulting to a peneplaned surface cut out of much younger, unconformable volcanics: the faulting in the marginal area of the basement rocks forms the eastern side of the Rift Valley. The basement rock adjacent to the zoisite-amphibolite is usually an amphibolite with conspicuous large, brown-red garnets. The occurrence of this garnet-amphibolite is usually an indication of the proximity of the zoisite-amphibolite.

The outcrops of the zoisite-amphibolite are small. The largest is just over 100 yards long and about 50 yards wide. The foliation corresponds with that of the surrounding metamorphic types. It is, therefore, difficult to determine whether the amphibolite is a highly altered intrusive rock or whether it has been formed by metasomatism or is a migmatic product. Probably each of these processes has played a part in its production.

The zoisite-amphibolite shows a continuous gradation from a very dark amphibolite containing very little zoisite to a much paler apple-green, zoisite-rich rock with little amphibole, but usually containing large, red corundum crystals. The schistosity of the zoisite-rich types is poorly defined. In thin sections under the microscope the rock shows the association of corundum, amphibole, and zoisite; a few sections show, in addition, a little plagioclase and colourless mica. There is also a secondary, partly fibrous product.

In addition to these amphibolites and zoisite-amphibolites the collection presented to the museum included one specimen of a white zoisite-rock; this is monomineralic and slightly coarser-grained than the green variety, with the same granular texture.

Corundum.—The corundum forms conspicuous ruby-red crystals up to 3 cm. in diameter, which frequently show hexagonal, idioblastic outlines. All the crystals show intense cracking and granulation, obviously the result of stress. This cracking has destroyed the otherwise gem quality of the mineral. Some crystals are riddled with small zoisite inclusions and contain, in addition, a few opaque grains, probably of iron-ore. An interesting feature is the frequent intergrowth with amphibole at boundaries of the two. The corundum grains then show no well-defined boundaries but rather a 'fretted' and complex perimeter with narrow tongues of amphibole radially arranged. The corundum shows a distinct pinkish tinge in micro-sections of the usual thickness.

Amphibole.—The amphibole usually forms irregular grains of variable size, the maximum length being about 0·4 mm. When associated with plagioclase, however, it sometimes shows small, sharply idioblastic diamond-shaped sections with the prism as the prominent form. Other grains show pinacoidal cleavages in addition to the prism cleavage, thus presenting a highly 'scarred' appearance and conspicuous relief. The mineral is pale in colour and is only faintly pleochroic.

The absorption is $\gamma - \beta > \alpha$, with γ and β blue-green, α pale yellow-green to almost colourless. The values of 2V and of $\gamma : c$ were determined on a Leitz 4-axis stage; and β by the immersion method, in sodium-light, on three selected grains showing the central emergence of an optic axis. The values of γ and α were determined by calculation from the values of β and 2V combined with the value of $\gamma - \alpha$, which was measured with a Berek compensator.

$2V\gamma = 82°$ (mean of 5 values: range 78–84½°).

$\gamma : c = 21°$ (mean of 5 values: range 19–22½°).

$\beta = 1{\cdot}648$ (mean of 3 values, 1·647, 1·648, 1·650).

$\gamma - \alpha = 0{\cdot}021$; α 1·639 (calc.), γ 1·660 (calc.); sp. gr. $d_4^{20} = 3{\cdot}13$.

These values, in conjunction with the relative lack of colour and feeble pleochroism, show that the amphibole is an iron-poor hornblende belonging to the tremolite-edenite series (about 45 molecular % edenite).[1]

[1] A. N. Winchell, Elements of optical mineralogy, 4th edit., 1951, pt. II, fig. 324, p. 433. [M.A. **11**–463.]

Plagioclase.—This is only sparsely present, being observed in only one of the half-dozen sections examined. It forms highly irregular grains up to 3 mm. in diameter, fresh and unzoned, enclosing many crystals of amphibole and zoisite. The grains show one set of fine twin-lamellae intersected at a small angle by a prominent cleavage. A second cleavage, nearly perpendicular to the first, is occasionally visible as ill-defined intermittent cracks. Measurement on the universal stage showed the twinning to be on the pericline law, the prominent cleavage to be (001), and the composition to approach An_{100}.

The angular values obtained were: $\alpha\alpha$, 102°, $\beta\beta$, 56½°, $\gamma\gamma$, 104°, $2V_\alpha$ 77½°. These angles, interpreted on Tertsch's curves[1] for calcic plagioclases, confirm the composition to be that of an anorthite (about An_{97}). The values accord reasonably well with those derived from the low-temperature curves for a plagioclase of this composition. Interpolation from Tertsch's high-temperature curves gives much less consistent An values. (The $\alpha\alpha$, and $\beta\beta$, values are beyond the ranges of the high-temperature curves.) In view, however, of the necessarily approximate determinations (one set of twin lamellae being too narrow for measurement save in one or two grains) and the possible doubtful accuracy of the high-temperature determinative curves,[2] the diagnosis of the low-temperature modification can only be regarded as tentative.

Zoisite.

The abundance of the zoisite and its unusual optical properties were considered to justify detailed chemical and optical examination. The mineral occurs in two forms—a common green variety and a colourless modification, the latter represented in only one rock-specimen. A chemical analysis of a gravity-separated, hand-picked sample of the green zoisite gave the results shown in table I.

The feature of the analysis is the low value for H_2O and the high values for Al and Ca. Even after recalculation to the basis of 52(O,OH) the cation total is about 3 % higher than that required to satisfy the formula $Ca_2Al_3Si_3O_{12}OH$. On the actual (empirical) O,OH content the cation total is 5% high.

[1] H. Tertsch, Zur Hochtemperaturoptik basischer Plagioklase. Tschermaks Min. Petr. Mitt., 1942, vol. 54, pp. 193–217. [M.A. **9**–270.]

[2] D. L. Reynolds, The difference in optics between volcanic and plutonic plagioclases . . . Geol. Mag., 1952, vol. 89, pp. 233–250. [M.A. **12**–137.]

TABLE I. Chemical analysis of green zoisite from northern Tanganyika.

(B.M. 1952,133.) Analyst, D. I. Bothwell.

		Atomic ratios.			Empirical unit-cell contents.[1]		Cell contents on basis of 52(O,OH).	
SiO_2 ...	39·16	Si	...	0·652		12·33		12·08
Al_2O_3...	33·50	Al	...	0·657	12·42		12·17	
Fe_2O_3...	1·75	Fe'''	...	0·022	0·42	12·92	0·41	12·66
FeO ...	nil							
Cr_2O_3...	0·33	Cr	...	0·004	0·08		0·08	
CaO ...	25·02	Ca	...	0·446	8·43		8·26	
MgO ...	nil					8·43		8·26
MnO ...	0·014	Mn	...	0·0002	0·004		0·004	
Na_2O...	nil							
K_2O ...	nil							
H_2O+	0·57	O	...	2·742	51·87	53·07	50·82	52·00
H_2O-	0·06	OH	...	0·063	1·20		1·18	
TiO_2 ...	0·001							
	100·40							

Sp. gr. (d_4^{20}) 3·364±0·005

Orientation.—Crystals of both green and colourless zoisites show a single cleavage. The cleavage cracks are truly plane, though rather widely spaced. Conoscopic observations on isolated crystals showed that α (= Bx_o) is in all instances perpendicular to the cleavage plane, which therefore corresponds to the $\gamma\beta$ plane. The orientation is, therefore, that of ferriferous zoisite with 5 % or more Fe_2O_3 (the β-zoisite of Termier).[2] Iron-free zoisite has the optic plane parallel to the cleavage; yet the analysis shows less than 2 % Fe_2O_3. Preliminary measurements of $2V\gamma$ showed values of about 25° for the green and 35° for the colourless varieties. These values correspond with those usualiy quoted for iron-free zoisite, i.e. 30°±. Both the colourless and green zoisites were found to have extremely strong dispersion with $r > v$. This dispersion, on the other hand, agrees with that given for a ferriferous zoisite. It is thus evident that the optics do not conform (in relation to the chemical composition) with those previously published for zoisite. The orientation and the dispersion indicate a ferriferous zoisite, while the optic axial angle suggests that the mineral has little iron, as confirmed by analysis.

In order to establish with certainty the relation between the optical and crystallographic directions three single-crystal X-ray oscillation photographs were taken by G. F. Claringbull about α, β, and γ. The layer-

[1] Calculated from the determined value of the sp. gr. together with the unit-cell dimensions a 16·30, b 5·60, c 10·21 Å. (L. Waldbauer and D. C. McCann, Amer. Min. 1935, vol. 20, p. 107.) [M.A. 6–179.]

[2] P. Termier, Bull. Soc. Franç. Min. 1898, vol. 21, pp. 148–170.

line spacings of the three photographs indicated the approximate values α 16, β 5, γ 10 Å. Comparing these values with those of Waldbauer and McCann it is evident that α coincides with a, β with b, and γ with c.

The cleavage is thus shown to be (100) and the optic axial plane is parallel to (010). At first sight the orientation of both these planes appears to differ from that of the textbook figures (for either iron-free or ferriferous zoisite), which show the cleavage as (010), and the optic axial plane as (010) for iron-free and (001) for ferriferous zoisite. However, the textbook orientations are based on axial ratios: $a : b : c = 0{\cdot}62 : 1 : 0{\cdot}34$, derived from the earlier morphological measurements.

Comparing these ratios with the X-ray parameters it is evident that:

a (from morphological measurement) $= c$ (from X-ray measurement)
b („ „ „) $= a$ („ „ „)
c („ „ „) $= b$ („ „ „)

Making these transformations (giving $a : b : c = 0{\cdot}625 : 1 : 0{\cdot}344$) it is apparent that the cleavage does, in fact, coincide with the (010) plane of the textbook figures and that the optic axial plane is the (001) plane of these authors. In other words, the orientation agrees with that given in textbooks for ferriferous zoisite.

Size and arrangement of crystals.—The green zoisite usually shows distinct elongation parallel to β, with partial alignment of the crystals. The length: breadth ratio is of the order of 3 : 1, but reaches 6 : 1 in some grains. The crystal length varies from about $\frac{1}{2}$ to $1\frac{1}{2}$ mm., but is sometimes reduced in proximity to the corundum crystals. The green zoisite shows few crystal faces; many grains show sub-rounded terminations. Transverse cracks are extensively developed and are a prominent feature.

The colourless zoisite, forming virtually a monomineralic rock, shows no elongation or schistosity. The grains tend to be equidimensional; the average diameter is 2 mm. (maximum 4 mm.). The grains form a polygonal mosaic and many show partial crystal form, though crystal faces often tend to be modified due to mutual interference during growth. All grains show an extensive system of cracks, sometimes roughly perpendicular to the cleavage, but often forming an irregular network. Five of the best-developed crystals in two sections of this colourless zoisite rock were measured on the universal stage in order to determine the faces represented. Each of the five resulting stereograms was first transposed, bringing γ to the centre. The five transposed stereograms were then superimposed to bring α, β, and γ into coincidence. Indexing of faces on this final stereogram was performed by plotting the poles on a

gnomonogram, based on the X-ray parameters, with γ (c) at the centre i.e. having the same orientation as the stereogram). The forms thus identified after transformation from the X-ray orientation ($\gamma - c$) to the morphological orientation ($\gamma = a$) are as follows:

(100) (vicinal face 8° from 100), (010), (021) (vicinal face 4° from 021), (034) (vicinal face 4° from 034), (041), (091), (140), (142), (144), (164), (311), (313), (431), (562), (971), (991), (20.5.2).

Of these observed forms only five (100), (010), (021), (041), and (140), are listed as crystal-forms by Dana and Goldschmidt. With the exception of (100) and (010), simple forms are absent and three faces are vicinal to faces having the quoted indices. (The angular differences in these instances are outside the range of experimental error.) The high indices may perhaps be due to mutual interference.

Optical properties.

Refractive indices.—The γ and β values of both the green and white zoisite were determined on selected oriented crystals, using the immersion method, with mixtures of methylene iodide and monobromonaphthalene. A Bellingham and Stanley refractometer was used to measure the refractive index of the matched liquid in sodium-light. The values of both γ and β were obtained from cleavage flakes, since the cleavage coincides with the $\gamma\beta$ plane. Cleavage flakes thus give a centred obtuse bisectrix interference figure and are easily recognizable. The value of β was determined, in addition, from grains showing the central emergence of an optic axis; grains having this orientation are also easily detected by their abnormal purple-yellow interference colours resulting from the extreme axial dispersion of the mineral.

For most of the refractive index measurements the 'control drop' method was used. The refractive index of the liquid mixture was adjusted to a value somewhat above the index to be measured in the mineral. The drop was split into two portions; the first portion remained on the glass slide (with the immersed grains) which was placed on the microscope stage. The second part of the drop was placed upon the glass prism of the refractometer which was immediately adjacent to the microscope, so that the two glass surfaces (carrying the two portions of the liquid drop) were separated by only a few inches. The operation was carried out in a room free from draughts. Owing to the more rapid rate of evaporation of the methylene iodide compared with that of the monobromonaphthalene, the refractive index of the two drops becomes

gradually lower. The liquid on the slide, therefore, slowly passed through the refractive index value at which it matched the desired index of the grain, and at this instant the refractometer reading was noted. This technique was found to give reasonably concordant values. For example, in one set of 8 measurements the difference between the maximum and minimum values was 0·0019, and was reduced to 0·0011 by omitting one reading.

The value of α was not determined directly, but was obtained by calculation from the mean values measured for γ, β, and 2V. Owing to the difficulty of finding suitable crystals having the required orientation, the theoretically derived index was considered to be more accurate.

Optic axial angle.—This was measured in sodium-light on the universal stage. Sections of about twice the normal thickness were used. Owing to the smallness of 2V the usual orthoscopic method was found to give wide fluctuations in the measurements and much more precise values were found to result from conoscopic observation (full apertures on substage diaphragms, and insertion of Bertrand lens). Four to five readings were made of the position of each optic axis. The values of 2V given in table II are the result of 12 determinations of the green zoisite and 12 of the colourless variety.

TABLE II. Optical data (mean values),

	α.	β.	γ.	$2V_\gamma$. range
Green zoisite	1·700	1·700	1·705	25° (17½–33°)
White zoisite	1·695	1·698	1·704	33½° (28–37°)

Dispersion.—It was apparent during the preliminary optical examination that the zoisite possessed extremely strong axial dispersion, since the isogyres of well-centred interference figures showed conspicuous colour fringes. It was, therefore, decided to attempt to measure the variation in the optic axial angle caused by changes in the wave-length of the light. Owing to the weak birefringence, the smallness of the crystals, and their extensive cracking, the accurate determination of 2V for light of varying wave-lengths presented some difficulty. The first measurements, made on an optic axial goniometer and on a stage goniometer, fitted to a Swift microscope, were not entirely satisfactory, although they confirmed the order of the dispersion (red to violet) to be about 10°.

It was finally found that much more reliable results were obtainable using a universal stage method. A suitably oriented crystal, giving one

almost centred optic axis, was isolated: both upper and lower surfaces were carefully ground, thus producing a parallel-sided plate about 0·7 mm. in thickness. This was mounted in a circular depression on a glass slide. A Leitz 4-axis stage was used for the measurements; the substage diaphragms were opened to give conoscopic definition. A Hilger

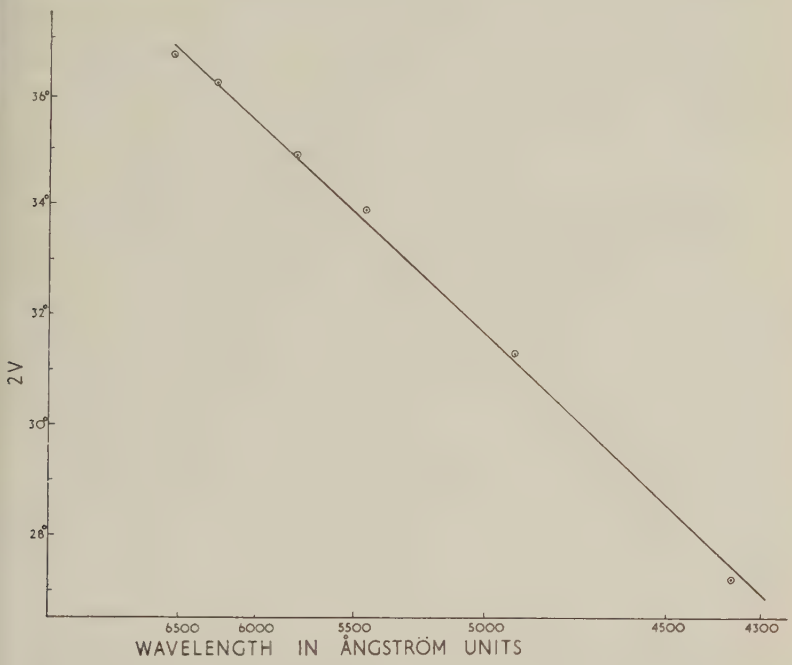

Fig. 1. Zoisite (colourless variety) from Tanganyika. Variation in optic axia angle 2V with wave-length of light.

monochromator was employed in conjunction with a high-pressure mercury-vapour 50 watt lamp, the emission from which was intense for the 'mercury violet' (4358 Å.) and 'mercury green' (5461 Å.) wave-lengths and satisfactorily strong for wave-lengths in the blue, yellow, and red orders of the spectrum. The value of 2V was determined for six different wave-lengths ranging from 4358 to 6550 Å. Using each eye alternately, 10 readings were made for the violet and blue wave-lengths and 6 readings for the remaining wave-lengths of the position of that optic axis which emerged almost vertically (A_1). Four readings were made of the other more inclined axis (A_2), which gave less precise definition of the isogyre. From these two sets of readings (for each optic axis)

the mean position of the acute bisectrix was determined. This angular value (Bx_a) was subtracted from the mean value obtained for A_1 for each wave-length, and the resulting angle was doubled, thus giving 2V. The corrections required for the difference in refractive index of hemisphere (1·649) and mineral (1·699), were very slight owing to the small inclinations. The resultant values of 2V for the six different wave-lengths are given in Table III. If a logarithmic horizontal scale (Hartmann dispersion paper) be used to plot these values, an almost straight line relationship results (fig. 1).

Table III. Zoisite (colourless variety) dispersion.

Wave-length.	Optic axial angle.
4358 Å.	27·2°
4916	31·3
5461	33·9
5790	34·9
6250	36·2
6550	36·7

Acknowledgements.—I wish to thank Dr. G. F. Claringbull for the X-ray data, Mr. D. I. Bothwell for the analysis, Dr. M. H. Hey for help with the indexing of the zoisite, and Mr. A. H. Weir for his assistance in some of the dispersion determinations. Details of the field occurrence were kindly supplied by Mr. N. J. Guest of the Tanganyika Geological Survey.

A note on the relationship between the precision of classical methods of rock analysis and the concentration of each constituent.

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[Read June 10, 1954.]

A GRANITE (G–1) from Westerley, Rhode Island, and a diabase (W–1) from Centerville, Virginia, were recently analysed by some 34 analysts in different countries for the purpose of obtaining thoroughly reliable rock standards for spectrochemical analysis. Most determinations were made by so-called classical methods of chemical analysis. The results of the investigation have been discussed by Fairbairn and others.[1] Fairbairn examined the results statistically and, using the relative deviation (standard deviation expressed as a percentage) as a measure of precision, concluded that precision deteriorated with a decrease in the concentration of a constituent. In the present paper this general observation will be demonstrated quantitatively by means of a graphical presentation, thus providing the petrologist with a guide for rapidly assessing and comparing the precision of classical methods of chemical analysis over considerable concentration ranges. This guide should apply particularly to rock analyses which have been made during the last 60–70 years.

For his statistical calculations, Fairbairn assumed normal (Gaussian) distribution of observations about some central (modal) value. Although replicate chemical determinations rarely follow such a distribution,[2]

[1] H. W. Fairbairn, W. G. Schlecht, R. E. Stevens, W. H. Dennen, L. H. Ahrens, and F. Chayes, A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks. Bull. U.S. Geol. Surv., 1951, no. 980.

W. G. Schlecht, Co-operative investigation of precision and accuracy. Anal. Chem., 1951, vol. 23, p. 1568.

H. W. Fairbairn and J. F. Schairer, A test of the accuracy of chemical analyses of silicate rocks. Amer. Min., 1952, vol. 37, pp. 744–757. [M.A. **12**–33.]

H. W. Fairbairn, Precision and accuracy of chemical analysis of silicate rocks. Geochim. Cosmochim. Acta, 1953, vol. 4, pp. 143–156. [M.A. **12**–264.]

[2] Positive skewness, negative skewness, irregular distributions, as well as normal and lognormal type distributions have been observed for the particular series of chemical observations under discussion.

statistical calculations based on assumed normal distribution for all constituents may nevertheless be used for the purpose of semi-quantitatively comparing precision in a general way, such as will be attempted here. The exact statistical nature of the distribution of chemical determinations for each individual constituent should, however, be taken

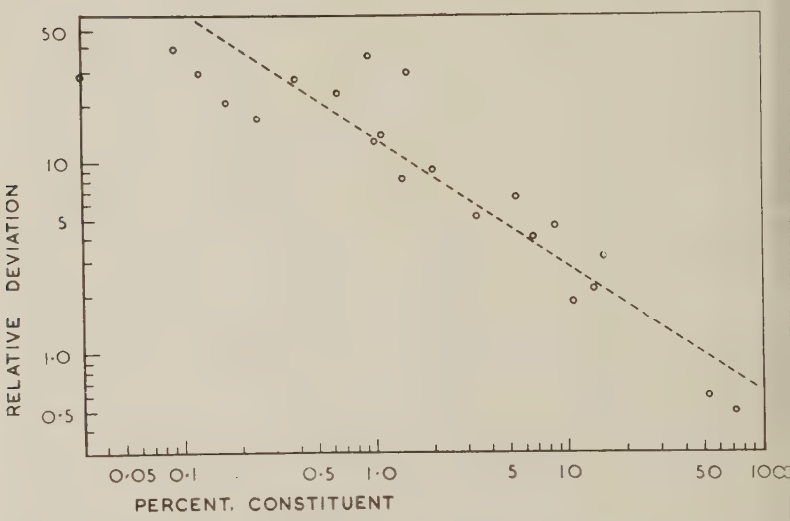

Fig. 1. The precision, as measured by relative deviation, of a chemical determination is related to the concentration of each constituent in granite (G–1) and diabase (W–1), using geometric scales; the regularity is quite well developed.

into account when making fully quantitative predictions: this becomes more important as the dispersion of observations increases.

As we wish to examine the relationship between the relative deviation (C) and the concentrations of several constituents over wide variations of both variables (concentration varies from 72·9 % SiO_2 in G–1 to 0·9 % P_2O_5 and C varies from 0·5 % to 39 %) log scales will be used. They have the advantage also of readily revealing a possible exponential relationship because this would appear as a straight line—fig. 1 happens to be a fair example.

Fig. 1 relates C (after Fairbairn, 1953) and percentage constituent (SiO_2, Al_2O_3, CaO, &c.) in granite G-1 and diabase W–1. The plotted points are purposely not labelled as the relationship in fig. 1 is intended to be perfectly general. The regularity is well developed and, in fact, hardly short of amazing when the variety of chemical procedures and the

range of concentration is taken into consideration. Thus, for example, most analysts determined Si, Al, Ca, Mg, and P gravimetrically, Fe volumetrically, Na and K by the Lawrence Smith procedure, and Mn and Ti by colorimetric methods. The slope of the curve of best fit is about 33°, the tan of which is 0·65 ; in other words, the general relationship may be expressed approximately by

$$C\alpha \frac{1}{\text{concentration}^{0\cdot65}}.$$

The value of the exponent would be unity had the slope been 45°.

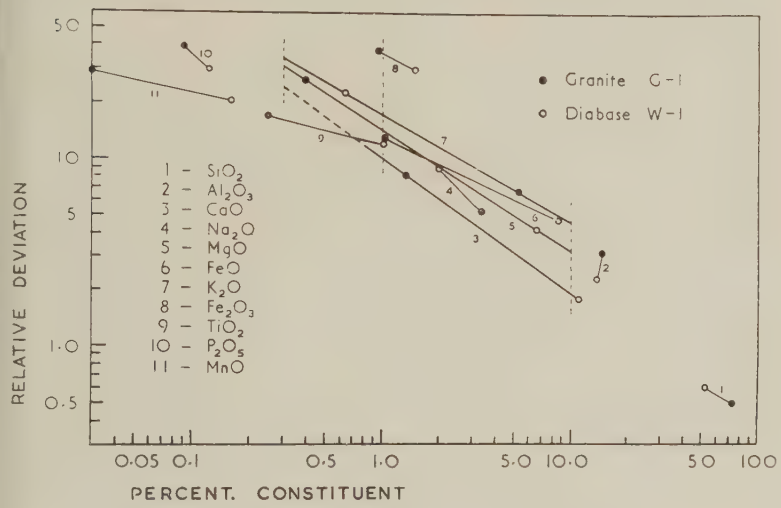

Fig. 2. As in fig. 1, but showing details of constituents.

Details for each constituent are shown in fig. 2. As in fig. 1 of Fairbairn (1953) this plot shows that precision deteriorates with decrease of concentration of each individual constituent, with the exception of Al_2O_3. It is of interest to note that the slopes of lines joining pairs of plotted points are often similar to the slope for the stream of points (cf. fig. 1) as a whole. As might be expected, the slopes of such lines for titanium and manganese are less than those of the others as these two elements are usually determined colorimetrically.

Figs. 1 and 2 may be of some aid to a petrologist for roughly assessing and comparing the accuracy with which individual constituents may be determined by means of classical methods of chemical analysis. Fig. 2 shows clearly that Fe_2O_3 determinations are conspicuously inferior to any

others at a given concentration (for example 1 %) and that lime determinations are decidedly superior to both potash and magnesia over the concentration range covered by W–1 and G–1. A fairly critical comparison involving some extrapolation may be made for some constituents, as indicated by CaO, MgO, and K_2O in fig. 2. Table I compares relative deviations for these constituents at 0·3, 1, and 10 % as obtained from the extrapolations in fig. 2.

TABLE I. A comparison of relative deviations at three different concentrations of K_2O, MgO, and CaO.

Concentration.	Relative deviation.		
	K_2O.	MgO.	CaO.
0·3 %	35 %	32 %	(25 %)*
1·0	18	15	10
10·0	4·8	3·3	2

* Very rough, as it is based on considerable extrapolation.

At a concentration of 0·3 % K_2O, as in olivine-basalt, for example, C is large (35 %) and indicates that there must be considerable error in many published determinations. Statistical prediction thus indicates that two-thirds of the determinations should fall within $0{\cdot}3 \pm 0{\cdot}1$ %, that is, 0·2 to 0·4 % K_2O, but that the remaining one-third would be outside these limits; 95 % of the determinations should fall within 0·1 to 0·5 % K_2O. It must be emphasized again that these calculations can only be regarded as approximate, particularly as they are based on assumed normal distributions; nevertheless, they should indicate the error magnitudes which are expected for different constituents at different concentrations. Caution must be exercised to confine such comparisons and calculations to classical methods of chemical analysis of rocks having a composition approximating granite or diabase, basalt and gabbro, or something intermediate.

The regularities of figs. 1 and 2 make an interesting comparison with spectrochemical methods where reproducibility remains independent of concentration. Figs. 1 and 2 also provide an example of the power of the geometric scale for revealing regularities which might otherwise remain hidden.

An occurrence of palygorskite in the Shetland Isles.

(With Plates XIV and XV.)

By I. Stephen, B.Sc., Ph.D.

Rothamsted Experimental Station, Harpenden.

[Read June 10, 1954.]

I. Introduction.

In May 1950 the writer received from Mr. Henry Burgess, of Spiggie, Shetland Isles, a specimen of a material which had been found by a local quarryman. The property of the material which had particularly attracted attention was that when it absorbed water it became soft and pliable and looked like wet leather. The specimen, measuring approximately $4 \times 2 \times 1$ inches, had a brownish iron-stained outer skin, and showed slight signs of foliation parallel to its length. Internally it consisted of a white to greyish-white compact material, in which were embedded portions of the syenitic country-rock. This white material has been shown to consist dominantly of the mineral palygorskite (attapulgite).

During the summer of 1952 the writer had an opportunity of visiting the site, and further specimens were found in situ, although the largest of these measured only about one inch.

II. Field relations.

The site where the palygorskite was found is the northernmost of four small quarries on the south-eastern flank of Noss Hill in South Mainland, Shetland Isles. The quarries, which are about $\frac{1}{3}$ mile WNW. of the farm of Bakkasetter, were being worked by the Zetland County Council for 'rotten granite' for use as road metal.

The exposed bedrock is a reddish coloured medium-grained syenite, which is markedly non-uniformly weathered, and is overlain by reddish sandy boulder clay of local origin, which in places is 10 or more feet thick. The rock has apparently been subjected to considerable hydrothermal alteration, as is shown by the presence of quartz-haematite veins, and epidote and epidote-haematite incrustations along joint planes. The palygorskite occurs in what appear to be roughly vertical crush-bands,

several yards wide, where the rock has a bleached appearance and is so highly altered that it is soft and friable and can be readily crumbled in the hand, and when wet is a non-plastic clayey grit. It is probable that the alteration in these zones is due to the action of hydrothermal solutions, as the rock is thoroughly decomposed at the lowest depths exposed (about 10 feet from the surface), whilst adjacent exposures of bedrock show a weathering crust only a fraction of an inch thick.

III. Mineralogy.

The fresh rock is composed of microcline-perthite, albite-oligoclase, orthoclase, quartz (rare), and normally less than 5 per cent. of ferromagnesian minerals. Usually it contains conspicuous elongated crystals of green actinolite, up to 5 mm. in length, which may be partially altered to fibrous pale olive-green nontronite. The amphibole and secondary nontronite invariably contain epidote as inclusions, and are often associated with granular aggregates of haematite and anatase. Epidote is a common constituent of the rock, being distributed throughout as yellow-green grains, often replacing felspar, and also occurring as veinlets, where it is often associated with haematite and quartz. Accessory minerals are apatite and zircon.

In thin sections of the decomposed rock the felspars show all gradations between relatively unaltered and completely altered grains, the albite-oligoclase being much more strongly attacked than the microcline. The epidote, haematite, and quartz remain unchanged, but the ferromagnesian minerals have been altered or destroyed. The clay occurs as a white to very pale greenish material, which has partially replaced the felspars, and also occurs in thin veins penetrating the decomposed rock. X-ray examination shows it to be a montmorillonoid giving a rational series of (00*l*) reflections corresponding to *d* (001) 17·7 Å. for the glycerol-treated material: application of the lithium-saturation test (Greene-Kelly, 1952) shows that it is montmorillonite and not beidellite or nontronite.

The palygorskite occurs sparingly in irregular pocket-like masses and thin veinlets in the montmorillonitized rock. In thin section the mass of the palygorskite shows an intimate felted texture, the small fibres being interwoven and knotted through each other: but, marginally and around fragments of included rock, the fibres show a marked directional texture with their long dimensions parallel to the boundaries. This effect is shown by mass extinction of the fibres under crossed nicols, and is

robably due to clay movement and compaction after formation. The bres have straight (or nearly straight) extinction, and positive elongation. It is possible to obtain from the mass of interwoven fibres an interference figure which shows 2V negative about 15°. The mean refractive ndex is 1·520±0·005, and the birefringence is low.

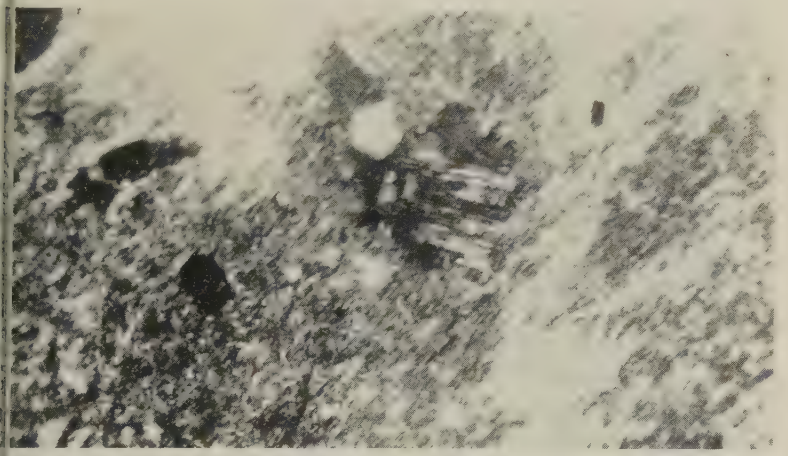

Fig. 1. Thin section of palygorskite, with included relatively unaltered plagioclase felspar. Crossed nicols. ×66.

The felspars occur as inclusions in various stages of alteration, from relatively unaltered grains (fig. 1) to completely replaced 'ghost' relics. The dominant feature is one of replacement, as relatively few unaltered grains are present. Numerous small crystals of high refractive index occur scattered throughout, and have the appearance of shattered epidotes.

IV. X-ray analysis.

In 1879 Heddle described under the name of pilolite a number of specimens of 'mountain leather' or 'mountain cork' from different localities and geologic occurrences. The similarity of pilolite to the Bakkasetter mineral and also to palygorskite occurring in mineralized granite at Tafraout, Morocco (Caillère, 1951), suggested the identity of these mineral types. It is interesting to note that one of Heddle's specimens also occurred in veins in decomposing granite at the Burn of Daugh, Cabrach, Aberdeenshire.

X-ray photographs of the Bakkasetter specimen, Heddle's pilolite

from the Cabrach, Aberdeenshire, pilolite (mountain leather) from Nawton, North Riding, Yorkshire, and mountain leather from Seaton, Devonshire,[1] are identical, and agree closely with powder data given by

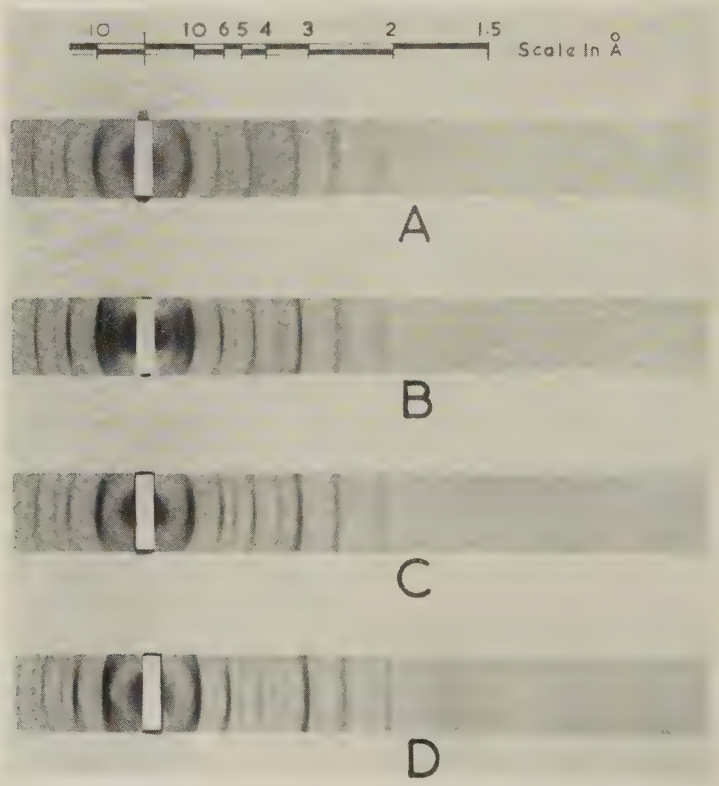

Fig. 2. X-ray diffraction diagrams of palygorskites: A, Bakkasetter, Shetland Isles, 2–0·5 μ; B, Bakkasetter, Shetland Isles, $< 0{\cdot}5\ \mu$; C, Cabrach, Aberdeenshire; D, Nawton, Yorkshire.

de Lapparent (1935) and by Bradley (1940) for samples of attapulgite from Attapulgus, Georgia, U.S.A. Reproductions of the X-ray photographs are given in fig. 2, except that of the Devonshire specimen which

[1] The specimens from Aberdeenshire, Yorkshire, and Devonshire were supplied by the courtesy of H.M. Geological Survey, London. The specimen (23789) from Seaton, Devonshire, occurs in fissures in the New Red (Keuper) Marl. Nawton, North Riding, Yorkshire, is in an area of Corallian rocks, and the matrix of this specimen (2952) is consistent with its having come from this source; it probably occurs in fissures in Corallian limestone.

showed the presence of gypsum in addition. The strongest line on the pattern at about 10·5 A. is distinctive, and readily distinguishes the palygorskites from the sepiolites which give a spacing at about 12 A.

Minor amounts of montmorillonite occur associated with the Bakkasetter palygorskite. The montmorillonite is concentrated in the finest size-fractions, and occurs only in minor amounts in the particle-size range greater than 0·5 μ (fig. 2, A and B). The X-ray pattern of the fine fraction also shows very faint lines at 7 A. and 3·5 A which can be ascribed to kaolin.

V. Chemical analyses.

A partial chemical analysis of the Bakkasetter mineral is shown in table I, col. 1, and is in good agreement with those of other palygorskites quoted in the literature (table I, cols. 2–4) except for the slightly higher value for alumina. This is probably due to the presence of small amounts of montmorillonite as an impurity.

Table I. Chemical analyses of palygorskite, &c.

	1.	2.	3.	4.	5.
SiO_2	52·35	51·17	51·00	54·04	51·52
TiO_2	—	—	—	0·32	0·48
Al_2O_3	15·44	13·73	12·89	9·83	17·15
Fe_2O_3	2·12*	1·55	0·09	3·52	5·65
FeO	—	0·31	2·68	0·19	0·32
MnO	—	—	0·08	—	—
MgO	6·60	6·40	7·54	9·07	2·80
CaO	0·14	2·89	—	1·69	1·72
Na_2O	—	—	0·27	0·08	0·15
K_2O	—	—	0·44	0·57	0·85
H_2O+	12·00	13·24	24·74	10·93	8·55
H_2O-	10·32	10·29		10·00	11·22
	98·97	99·58	99·73	100·24	100·41

* Total iron determined as Fe_2O_3.

1. Palygorskite, Bakkasetter, Shetland Isles. Analyst, C. Bloomfield.
2. Palygorskite, Nijni-Novgorod, Russia. (Caillère, 1936.)
3. Pilolite, Cabrach, Aberdeenshire. (Heddle, 1879.)
4. Attapulgite, Attapulgus, Georgia, U.S.A. (Kerr et al., 1950.)
5. Montmorillonite, Amory, Mississippi, U.S.A. (Kerr et al., 1950.)

The analyses of palygorskites show a marked resemblance to those of montmorillonites, particularly in their water-contents (cf. table I, col. 5). The main difference is that in the palygorskites magnesia is present in excess of the amount normally present in montmorillonites, and as a group they appear to lie between beidellite-montmorillonite and the

magnesium-rich clay minerals such as sepiolite (meerschaum) and saponite. Bradley (1940), however, has concluded that attapulgite has an amphibole-type structure, thus confirming an earlier suggestion by Nagelschmidt (1938) that in these minerals, channels of water between amphibole-like chains play the part of the inter-layer water in montmorillonites.

The exchangeable cations present in the palygorskite and in the associated altered syenite were determined spectrographically after leaching the samples with neutral normal ammonium acetate. These data and the experimentally determined values of the total exchange capacity are given in table II.

TABLE II. Exchangeable cations in milligram-equivalents.

	1.	2.	3.
Ca	5·80	n.d.	6·00
Mg	27·60	n.d.	16·30
Mn	0·11	n.d.	0·03
K	0·86	n.d.	0·29
Na	1·02	n.d.	0·46
	35·39		23·08
Exchange capacity	35·9	27·4	23·4

1. Palygorskite, Bakkasetter, Shetland Isles.
2. Pilolite, Cabrach, Aberdeenshire.
3. Montmorillonitized syenite, Bakkasetter, Shetland Isles.

Assuming that the palygorskite (table II, col. 1) contains 10 % montmorillonite of exchange capacity 90 m.e. 100 g., the exchange capacity of the palygorskite is 30 m.e./100 g., which corresponds closely to the value obtained for the sample from the Cabrach (table II, col. 3), but is slightly higher than data given by Caldwell and Marshall (1942), who report values ranging from 18 to 25·3 m.e./100 g. for samples of the attapulgite clay.

VI. Differential thermal analysis.

The thermal curve given by the Shetland palygorskite is shown in fig. 3, together with published curves of other palygorskites given by Syromyatnikov (1946) for a specimen from the Gorky region, U.S.S.R., and by Caillère and Hénin (1947) for specimens from Attapulgus, Georgia, U.S.A., and Taodeni, Sahara.

All these thermograms are characterized by two endothermic reactions in the low-temperature region at about 200° C. and 300–350° C., and

another endothermic reaction at 500–550° C. In addition the Taodeni mineral shows a well-marked endothermic peak at about 750° C. The

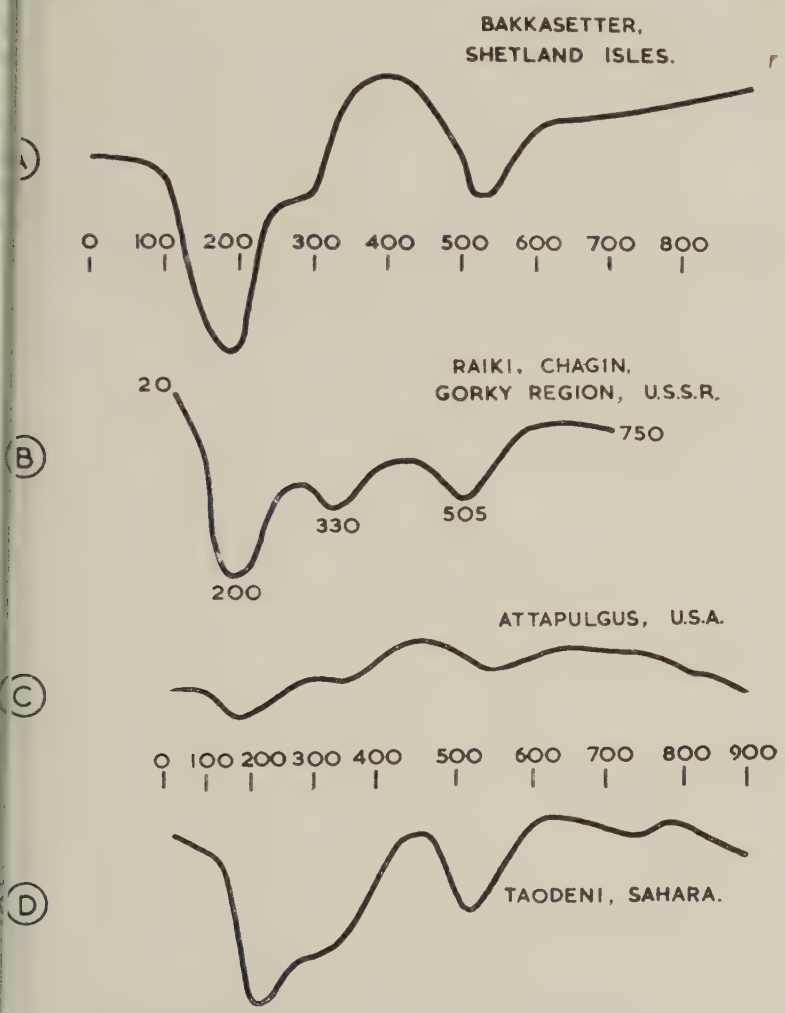

FIG. 3. Differential thermal analysis curves of palygorskites.

first very marked peak on the thermograms almost certainly corresponds to the loss of interstitial or sorbed water, and the higher peak at 300–350° C. probably corresponds to the 'less mobile' water which occurs associated with magnesium or aluminium in octahedral co-ordination in

the structure proposed by Bradley (1940). The marked peak at 500-550° C. would correspond to the loss of structural (OH) groups, and it is noteworthy that X-ray diagrams of palygorskites heated above 400° C show a marked modification, the strong spacing at about 10·5 A. being replaced by a diffuse halo and the other lines on the diagrams also being considerably altered.

VII. Electron micrographs.

The extremely fibrous nature of the Attapulgus clay has been demonstrated by Marshall et al. (1942), and electron micrographs of the British palygorskites studied reveal a similar development of crystal habit. The Shetland palygorskite (pl. XIV, A) occurs in bundles of extremely elongated lath-shaped crystals. The broader laths are seen to be parallel aggregates of smaller units, which give the appearance of striations parallel to the length, and cause step-like terminations at the ends, although the ends of individual laths are fairly regular. It is probable that the smaller units result mainly from the cleavage of the broader laths. The average breadth of the units appears to be about 30 mμ. The laths must be very thin, as, when they overlap, the outlines of the underlying ones can easily be seen. Evidence for the presence of a tubular structure, such as occurs in halloysite, is lacking.

The micrographs of the other palygorskites exhibit similar characteristics showing single laths and bundles of laths, together with mineral impurities of an entirely different habit in the Cabrach and Devon specimens (pl. XIV, B and XV, B). In the micrograph of the Devon palygorskite it is probable that the additional material is mainly gypsum, as this has been shown to occur finely admixed with the palygorskite.

VIII. Discussion.

The palygorskite described in this paper occurs in association with montmorillonitized syenite. The exchange complex of the altered syenite, in agreement with the occurrence of magnesium-bearing clay minerals, is saturated dominantly with magnesium ions, and it seems clear that the alteration involved the introduction of magnesium solutions from elsewhere than the parent-rock. In the field the juxtaposition of highly decomposed and essentially unweathered syenite suggests that the alteration of the rock is not due to atmospheric weathering, but to the action of hydrothermal solutions, which have permeated the rock mass subsequent to its emplacement, and which have preferentially acted along zones of weakness, such as crush-bands or shear-zones.

A hydrothermal mode of origin has also been suggested by Caillère (1951) for palygorskite occurring in granite at Tafraout, Morocco, but it should be noted that many of the occurrences of this mineral are under conditions which preclude this mode of formation. Perhaps the commonest occurrences are in association with calcareous sediments, in situations where montmorillonite would be expected. Probably a particular chemical composition of the system, especially in regard to the relative abundance of magnesium and aluminium, is the controlling factor in the formation of these minerals.

Note on nomenclature.—The name *palygorskite* has been adopted in this paper, as it was first used to describe these minerals by Ssaftschenkow (1862). The name was taken from that of a mining district in the Urals. In 1879 Heddle described (with chemical analyses) minerals known as 'mountain leather' or 'mountain cork', and showed that specimens from several localities in Scotland and from different geologic environments had closely similar physical characteristics and chemical compositions, and should therefore be regarded as a definite mineral species. He suggested the name *pilolite* (πῖλος, felt) because of their felted character. Friedel (1901, 1907) described similar minerals occurring in the Haute-Loire and the Pyrénées-Orientales under the name of *lassallite.*

Fersman (1908, 1913) defined the palygorskite minerals, mainly from their chemical composition, distinguished them from the sepiolites, and also classified pilolite and lassallite with the palygorskites. The term *attapulgite* was introduced by de Lapparent (1935), who studied specimens from Mormoiron, France, and Attapulgus, U.S.A., but a comparison of their properties with those of the palygorskites shows no significant differences. In view of this it is suggested that the name attapulgite should be discontinued.

Acknowledgements.—I am indebted to Mr. H. L. Nixon, Plant Pathology Dept., Rothamsted Experimental Station, for the electron micrographs. Thanks are also due to my colleagues Dr. C. Bloomfield for the chemical analysis, and to Mr. H. H. Le Riche for the spectrographic estimation of the exchangeable cations.

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Explanation of Plates XIV and XV.

Electron micrographs of palygorskite.
(Reduced about $\frac{2}{3}$ from the magnifications indicated.)

Plate XIV.

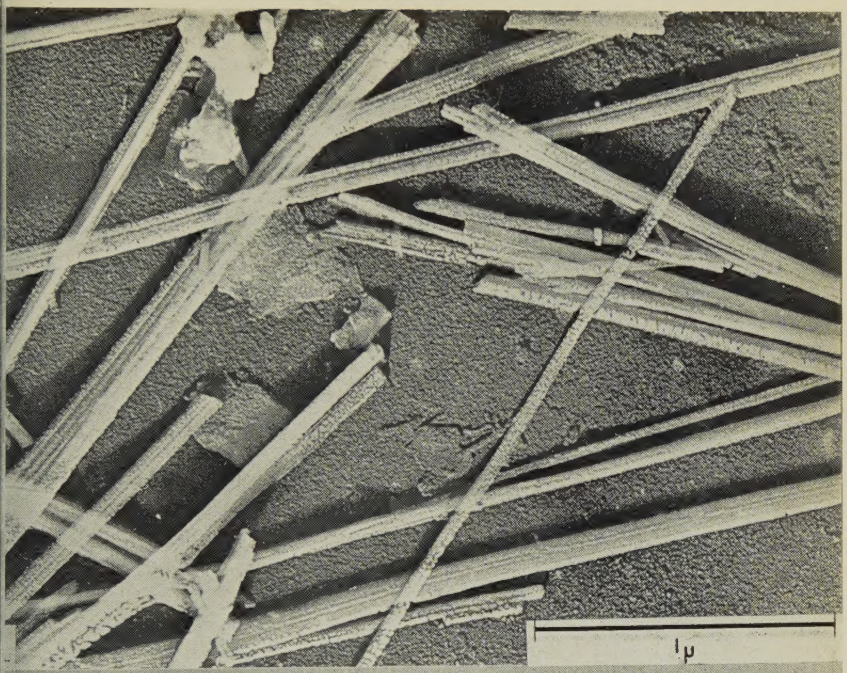
Fig. A. Bakkasetter, Shetland Isles. ×60,000.

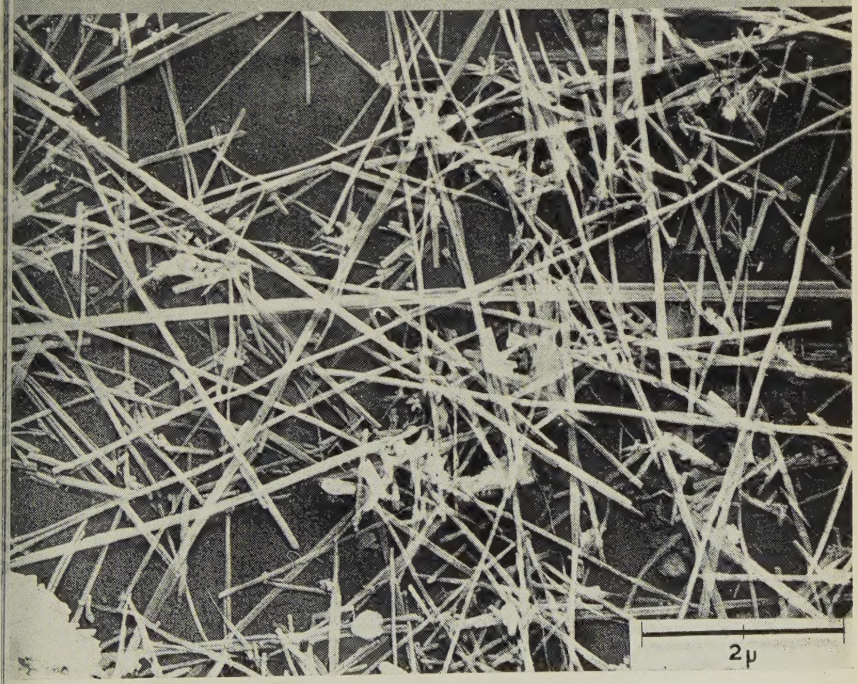
Fig. B. Cabrach, Aberdeenshire. ×20,000.

Plate XV.

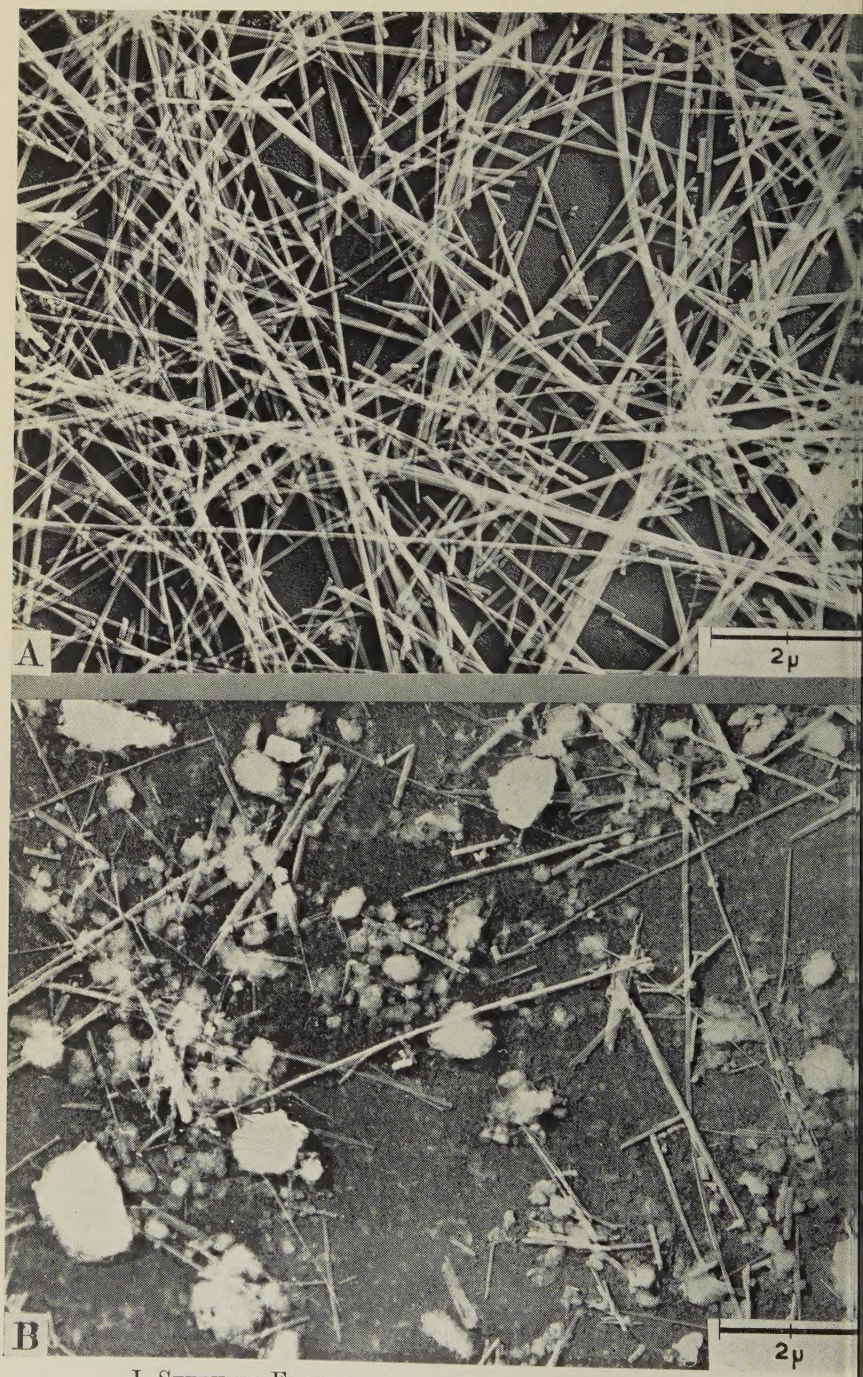
Fig. A. Nawton, North Riding, Yorkshire. ×15,000.

Fig. B. Seaton, Devonshire. The white patches are probably gypsum. ×14,000.





I. Stephen: Electron micrographs of palygorskite



I. STEPHEN: ELECTRON MICROGRAPHS OF PALYGORSKITE